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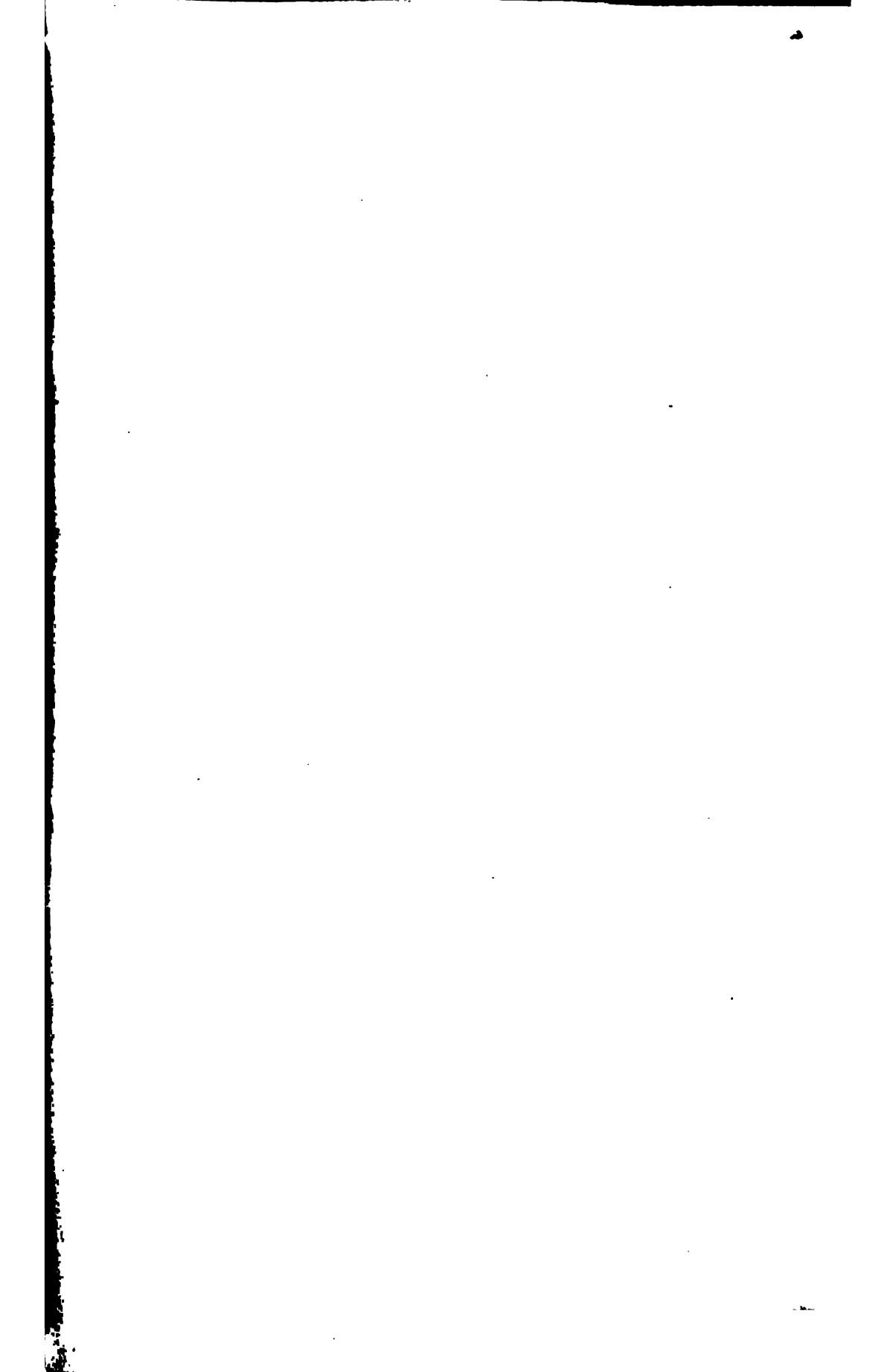
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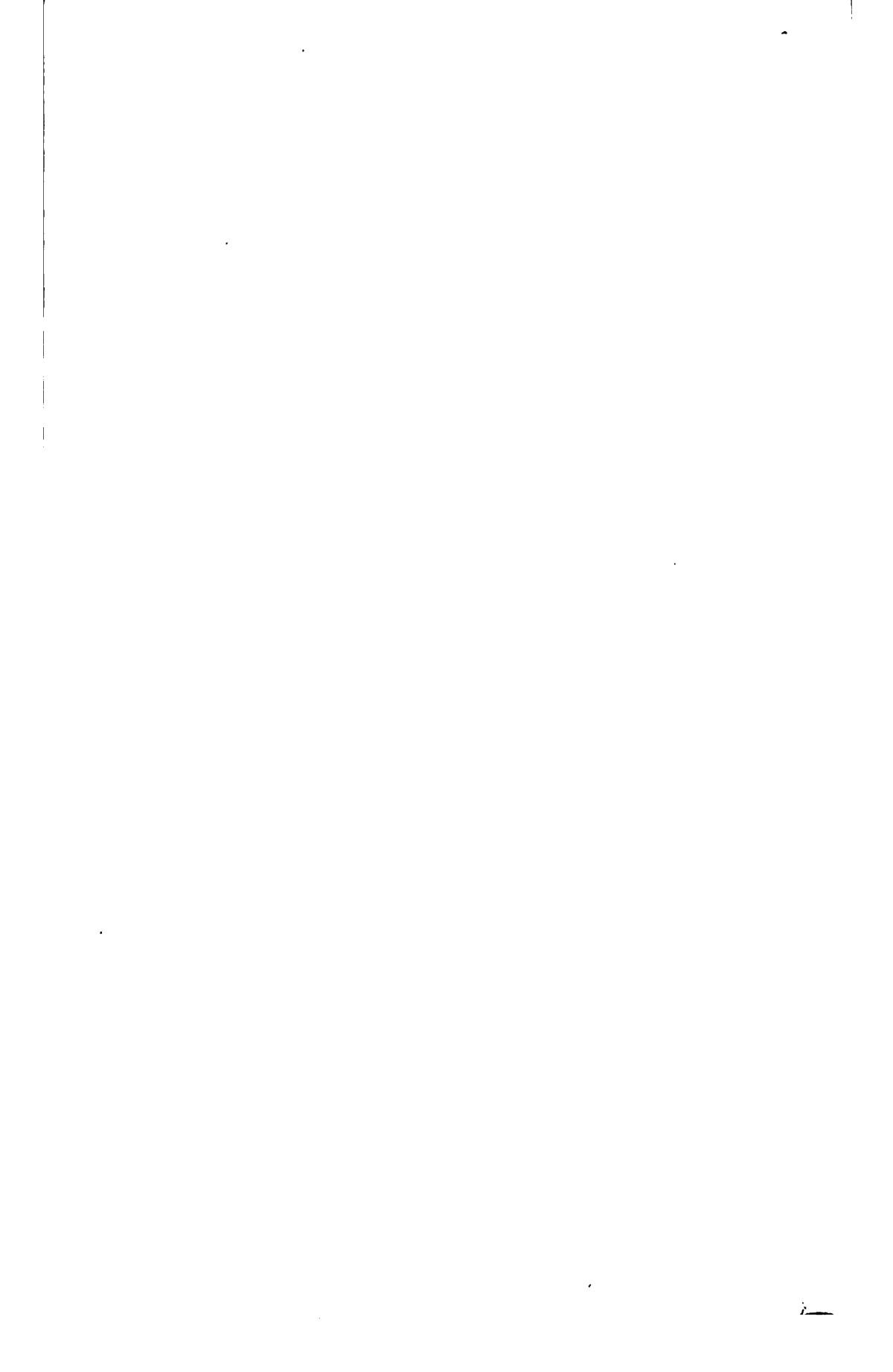






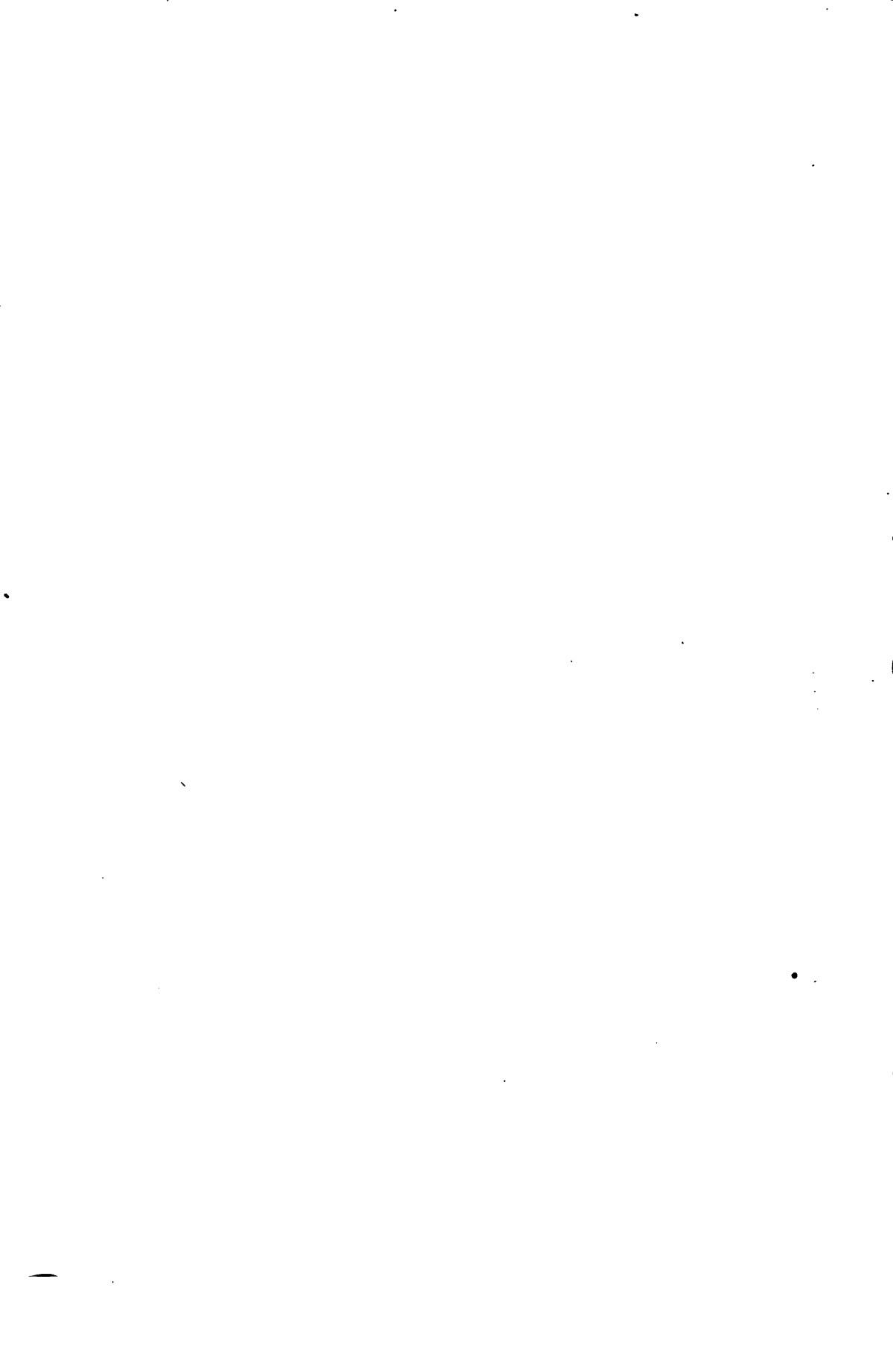








**The Collected Writings of  
Hermann August Seger**



# THE COLLECTED WRITINGS OF HERMANN AUGUST SEGER

Professor at the Royal Technical Institute, Berlin  
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Factory, Berlin

PREPARED

From the Records of the Royal Porcelain Factory at Berlin  
BY  
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MEMBERS OF THE AMERICAN CERAMIC SOCIETY

EDITED BY  
ALBERT BLEININGER, B.Sc.

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VOLUME I

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## PREFACE TO THE GERMAN EDITION

The reputation which the work of Seger enjoys in technological circles and the value which is attributed to it with reference to the clay industry, far beyond the boundaries of Germany, have caused in us the desire to facilitate the study of his writings by contemporary and future technologists by making a systematic compilation. The various essays were scattered through many volumes of the *Notizblatt* and the *Thonindustrie-Zeitung*, which latter journal was founded by the departed Dr. Aron and part of them were incorporated in the records of the Royal Porcelain Factory. Access to the latter was granted us by the director of the institution, Dr. Heinecke, with gratifying kindness and which otherwise would not have been open to the public.

In arranging the writings, literal reproduction of the various essays was always aimed at, and they were sifted only where repetitions were met.

It is our hope that by publishing "The Collected Writings of Hermann August Seger," which we have attempted to arrange according to the different branches of the clay industry, we have served not only German technology and research, but have also erected a monument to our late teacher and friend taken away from us so soon.

The work is published under the auspices of the "German Society for the Manufacture of Brick, Clay Wares, Lime and Cement," of the "Union of the Ceramic Industries of Germany," and the "Association of German Manufacturers of Refractory Products."

We thank all who have aided us in this undertaking, especially Dr. Heintz, at Sarau, and the Association of German Manufacturers of Refractory Products.

May the work become a source of inspiration and study to many.

DR. H. HECHT and E. CRAMER.

BERLIN, December, 1895.



## PREFACE TO THE AMERICAN EDITION

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The Publication Committee of the American Ceramic Society takes peculiar pleasure and satisfaction in presenting to the English-speaking public this translation of the writings of Dr. Hermann August Seger.

The circumstances under which this volume has been published are unusual in several respects. The Society undertook the task at its first session, while still numerically weak, and before it had existed long enough to develop much internal cohesion or any settled policy. That this work has been carried on during the process of evolution of the Society, without any serious breaks in continuity, is in itself remarkable.

Further, the translation of so large a volume by a number of widely scattered individuals, each working alone, and without the inspiration of frequent association, is certainly a noteworthy performance.

Add to this the fact that at no time has there been any financial return in view, either to the individual or to the organization, and that the work of translation has been practically all gratuitous, and the difficulty of the labor may be better understood, and its successful termination more fully appreciated. Seldom has a scientific organization given a more convincing proof of altruistic purpose in its work, than in this case.

Whatever of credit attaches to this work, however, must be given largely to the editor. To his industry and enthusiasm, and his technical acquirements, the success of the enterprise is largely attributable. It affords the committee the greatest pleasure to render this acknowledgment of the value of his services.

Of the book itself, it need only be said that in the opinion of the committee, it fully justifies the many sacrifices which its translation and publication have cost. Though it is only a compilation of articles written at irregular intervals during a life of

incessant toil, and written without any coherent purpose or thought of book-making, nevertheless it stands to-day, unchallenged, as the earliest satisfactory exposition of the principles of ceramic manufacture. In fact, Dr. Seger was the pioneer who first blazed the way, along which all must travel, who hope to reach the mastery of the fictile art, or who hope to convert it from an empirical handicraft into a systematic and scientific industry.

The committee feels that the American Ceramic Society has chiefly honored itself in thus honoring the memory of Dr. Hermann August Seger.

(Signed)      EDWARD C. STOVER, *Chairman*,  
                  HERBERT A. WHEELER, E.M.,  
                  STANLEY G. BURT,  
                  EDWARD ORTON, JR., E.M., *Secretary*,  
                  *Committee on Publication.*

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## The Life of Hermann August Seger

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PROF. CHARLES W. MESLOH, TRANSLATOR

Hermann August Seger was born on the 26th of December, 1839, at Posen, where his father, Karl Friedrich Seger, was Appellate Judge. After acquiring the necessary preparation in the municipal "Realschule" of his native city he attended the Provincial Technical Institute at Frankfurt-on-the-Oder, from which he graduated. In the year 1859 he attended the Royal Technical Institute at Berlin, where he zealously devoted himself to the study of chemistry under Rammelsberg, and later under Baeyer. In the inorganic laboratory Dr. Schöne, who has rendered a great service to the clay ware industries through his washing apparatus, was engaged as assistant, and there was a circle of fellow-students, from which, besides our master, many a name famous in our industry and its allied branches has gone forth. Besides Dr. Aron, co-founder of the *Thonindustrie-Zeitung* and an intimate friend of our beloved departed, I mention Dr. Hertzog, first chemist, then Director of the Royal Porcelain Factory in Berlin, who was also a very dear friend of Prof. Seger, and like him died far too soon; furthermore, A. Bernoulli in Eberswalde, F. Pernet, Director of the Birkenwerder Brick Company, Thieriot in Kaiserslautern, E. Peters, business manager of the Society of German Engineers, Dr. Zwick in Berlin, and the widely known chemists Dr. C. Heintzel in Lüneburg, and Dr. W. Michaelis in Berlin.

After graduation, Seger, equipped with thorough knowledge, turned to technology and undertook first the management of the alum and vitriol works Kreuzkirche at Neuwied on the Rhine. After several years of successful activity and now in possession of practical knowledge, he was graduated from the University of Rostock in the year 1868 and entered a chemical factory in Sweden for a short time.

In the meantime there had occurred in technology a series of events calculated to produce great revolutions in the most various arts. I notice especially the ingenious discovery of the continuous kiln by Hoffmann, at that time State Architect (1858), the introduction of gas-firing by means of generators and the use of steam in the manufacture of brick and other clay wares. Besides the youthful cement industry, which began to develop rapidly after the removal of the prejudice against home wares in Germany, it was above all the clay ware industry that was benefited by the invention of the continuous kiln and the various machines displacing each other in rapid succession. The increased technical needs

going hand in hand with these innovations, which brought the chemists face to face with new problems, excited their interest in a high degree.

So in 1869 Seger decided to devote his knowledge, his work, and his life wholly to the service of the clay industries.

After he had been practically engaged at home in a number of clay ware factories, and had made himself familiar with the needs of the various works and the demands made on raw materials and products from the standpoint of the practical man, he went to Belgium, England and Hungary—countries whose products were at that time far superior to the German productions—for the study of the various branches of the industry.

On his return to the fatherland he became connected with the never-to-be-forgotten Albrecht Konstantin Türrschmiedt and Friedrich Hoffmann. In the laboratory of the *Deutsche Töpfer und Ziegler-Zeitung*, founded by Türrschmiedt in 1869, he soon became an indispensable, a sincere admirer and a true friend of Türrschmiedt. Mutually inciting each other they passed their days together at hard work, and the annals of the *Notizblatt*, published since 1865 by the *Deutscher Verein für die Fabrikation von Ziegeln, Thonwaaren, Kalk und Cement* and edited by Türrschmiedt, give evidence of the esteem in which Seger was held by his master, and the warmth of the relations between them. How often in his lectures before the society he speaks with evident love in sincere words of this or that observation of his friend Seger! In the *Notizblatt* appeared in the year 1870 the first preparatory greater works of Seger, treatises of a theoretical character: "The Weathering Process of Crystalline Rocks and its Influence on the Structure of Argillaceous Formations," and "Crystallization and its Significance for the Clay Industries,"—treatises which beside their scientific character show a large number of the closest observations on the nature of clays and give a prophetic view of the problems to be solved in order to free the clay industries from empiricism. If we call to mind what value Türrschmiedt very properly laid on the knowledge of the structure of clays, with what devotion, with what acumen he drew this into the field of his observations, nothing is so well fitted to give us an insight into the relation of teacher to pupil as to see how completely Seger made Türrschmiedt's ingenious observations his own. To us younger men, who have been trained to study the history of this work from the beginning after Seger had achieved success, his great talent for the recognition of the needs of the clay industries is clear from his first works. With what clearness and certainty of aim he argues the necessity of the observation of the physical properties of clay; the study of the structure, plasticity, power of absorbing water, contraction in drying and burning, shape and size of the grains of sand and rock-flour, the peculiarities of concretions!

Unfortunately the days of happy work were suddenly interrupted by the early death of Türrschmiedt. But if ever prophetic word was fulfilled, it was the word of Friedrich Hoffmann when, on the 25th of January, 1872, he proposed to the above-mentioned society to appoint Seger as editor of the *Notizblatt* since "he looks upon the study and the furtherance of the ceramic industry as the work of his life."

In addition to his work as editor of the *Notizblatt* Seger undertook the editing of the *Deutsche Töpfer und Ziegler-Zeitung* and the management of the laboratory connected with the latter with the assistance of Dr. Aron, the friend of his student days. In accordance with Türrschmiedt's bequest we see the two friends busied with the investigation of the physical properties of clays by means of the washing analysis and with investigations concerning the causes of the coloring of bricks.

In 1872 the *Notizblatt* publishes a series of letters of travel in which the deceased gives his views concerning a large number of methods of manufacture which he studied at the factories themselves, both at home and abroad. The content of these letters was of the greatest importance especially for that time, in which by the introduction of the continuous kiln and machinery a gradual transition to the production on a large scale of bricks and terra cotta took place, and when also in allied branches of the clay industries a decided advance began to show itself.

The reports of the deceased on the International Exposition at Vienna (1873) have a similar importance. In these and in his letters: "Concerning Oldenburg Clinkers," "Brick-making along the Lower Rhine and in Belgium," "Brick-making in England," "On the Production of Black Clinkers," "Notes on the Production of Pressed Bricks from Pulverized Clay," we are informed not only concerning the details of the various methods of manufacture and the use of the products, but also concerning the economic conditions of the branches of industry in question, so that the German manufacturer could learn much from this picture of foreign industry. It may be added to the honor of the German manufacturers of clay wares that the reproach of "less intelligence" as compared with their English brethren is hardly justifiable to-day.

Compare the reports concerning the Nassau Pottery District with those concerning the potteries of Staffordshire. What recognition he gives to the pottery schools (Wedgwood Institutions) in Burslem, Stoke and Etruria, which were founded and are kept up by voluntary contributions without assistance from the state, which are provided with libraries and museums, and in which are taught all the arts and sciences that seem helpful to the pottery business! But how was it with instruction in these lines in Germany at that time? Pioneer work had to be undertaken and completed, a ceramic science had to be created, before advice and instruction could be given.

It was soon found, in the case of Hoffmann's continuous kiln, that it would not do simply to fill up the kiln and fire away, but that the water-smoking process had to be carefully watched, and that the production of buff-face bricks from materials containing lime was connected with great difficulties. It remained for Seger to explain the phenomenon of discolorations on bricks. The new method of water-smoking in which dry warm air from the burned divisions is used, as well as the new manner of burning in which a reducing flame is produced by means of a reversed draft, how simple and ingenious they were in their management, how great in their results!

It has always been the way of great men to be plain in their intentions. Only the charlatan is pleased by subtleties. How often Seger modestly, unconscious of his true greatness, admonished his pupils never to make anything too elaborate when questions were put to him in regard to correcting sources of faults in manufacture. Thus his propositions for the burning of buff bricks from clays containing lime rest on the simplest manipulations possible, based on the observation that with a prevailing oxidizing flame the sulphur vapors appearing in the fire-gases change the calcium carbonate in the bricks into gypsum and prevent its union with the weaker silicic acid while in a flame, temporarily strongly reducing, the sulphuric acid is volatilized as sulphurous acid and the ferriferous silicates of aluminium are caused to form yellow silicates with the lime. This observation and the manner of burning based on it has made the continuous kiln popular, for however highly the great saving of fuel, going as high as 60 percent, as compared with the periodic kilns, was valued, it was intolerable for a large number of factories to be able to burn only red, flashed, spotted ware instead of the accustomed buff brick. What we do not read in the papers of that time the contemporaries know: how Seger, at the request of Hoffmann, hastened from plant to plant to introduce the new process of water-smoking and the burning of buff bricks in the continuous kiln and to reestablish the strongly doubted claim of the continuous kiln as a suitable kiln for the burning of face-bricks.

In the meantime the work in the laboratory had made good progress; Aron's beautiful treatises concerning the plasticity, shrinkage and other fundamental properties of clay caused by the form of the clay particles (1873) and concerning the effects of non-plastic ingredients in clays (1873) must be mentioned here; Schöne's washing apparatus, although not perfect, proved an instrument of very great value in the hands of proper observers. But it was soon found that the clay substance separated by means of this instrument from the coarse and fine sand and rock flour was not to be considered as such in a chemical sense as it had been characterized in a few cases relating to the discovery of the formula

of kaolins on the basis of a rational analysis, but that only in a physical sense it is to be looked upon as clay substance, as the bearer of the plasticity. This circumstance led Aron to the idea of introducing the rational analysis for the investigation of all clays, *i. e.*, to separate it into compounds chemically united in themselves.

The hopes connected with this method of investigation we see fulfilled subsequently in the most brilliant manner. The two friends had frequently spoken of the uselessness of the ultimate analysis of clays for the ceramic industry and had sought a means for the better understanding of the constituents of clay in the washing analysis; only the rational analysis, by means of which the proportion of real clay substance, of quartz and feldspar in clays, could be found gave the desired clearness concerning the questions at issue.

In the files of the *Notizblatt* for the year 1876 we find the great essays of Seger concerning "The Constitution of the Plastic Clays and the Kaolins" and with it at the same time the proof of the eminent importance of the rational analysis for the knowledge of the composition of the various clay products, be the ware porcelain, white ware, stoneware, or of a different nature. From now on the really speculative search after a suitable composition of bodies for finer clay products begins, and it is to be looked upon as an indisputable fact, that through Seger's lead the rational analysis has given its present position to finer ceramics.

We will not conclude this period of activity of our dear master without a look into his private life and to mention his marriage to Mrs. Emma Schur, *née* Schmidt, on the 11th of September, 1875, an event which gave to his life an abundance of happy days and to his mind the power of facing calmly the vicissitudes in human affairs to which we are subject.

In the year 1877 Seger gave up his position as editor of the *Notizblatt* and, to make his life independent, founded the *Thonindustrie-Zeitung*, together with Aron. On account of the importance which was even at that time attached to his work for the clay industries, which henceforth appeared in this paper and the confidence which everybody had in him, the undertaking could not fail. In the first number of the *Thonindustrie-Zeitung* of the 2nd of December, 1876, the most prominent ceramists, among others, Dr. C. Bischof, A. Bernoulli, A. Bleichert, Otto Bock, Dr. Boehme (later director of the Royal Prussian Experimental Station for the Testing of Building Materials), Bues, Dr. Cohn in Martinikenfelde, A. Hausding, Dr. A. Heintz, Dr. C. Heintzel, Dr. Herzog, Hillig, Kägeler, Dr. R. Kayser, of the Bavarian Industrial Museum in Nürnberg, Liebold, Lietzmann, G. Mendheim, C. Nehse, E. Peters, W. Reid in London, J. F. Rühne, Dr. Sarnow, chemist of the Royal Porcelain Factory in Berlin, Schepky, F. Steinmann, Wesenberg, Dr. K. Wilkens, G. Zell, and Dr. Zwick had promised to publish their work in this periodical.

The thorough study of the technology of the continuous kiln with the use of the most different clay materials was set forth in 1877 in a treatise by Seger, entitled "Concerning the Position of the Continuous Kiln in the Clay Industries," in which the color phenomena of the yellow burning, calcareous clays like that of Birkenwerder, the red burning, ferriferous clays, low in lime like that of Rathenow, the yellow burning lignite clays, low in iron and containing no lime, of the class of the Greppin-Bitterfeld materials, and the white burning kaolin-like clays rich in alumina and low in iron, under reducing and oxidizing conditions in the presence of sulphuric acid or free from it, have been set forth in the most thorough manner. The exact knowledge of the phenomena discussed in this essay is still of immense value to the brick burner, and a close observer will obtain much information in regard to the remedying of defects from the study of these statements, especially when he is able to keep a check on the fire by means of gas analysis and pyrometric cones. For this purpose the departed worked out a suitable method for the investigation of industrial gases (1878) and discussed the effect of fire-gases in the kilns of the ceramic industry as well as the distribution and composition of the gases in kilns (1879). The cones will be spoken of later.

On account of the esteem in which the deceased was held far beyond the limits of the "German Society for the Manufacture of Bricks, Clay Wares, Lime and Cement," it was but natural that the Prussian government at the founding of the Chemical-Technical Experiment Station at the Royal Porcelain Factory at Berlin secured his cooperation, especially as the director at that time, Privy Counsellor Möller, who knew how to keep in touch with the industries, had long ago taken the greatest interest in Seger's unusual talents for the investigation of the foundations of the clay industries. Möller accordingly made the following report to the Minister of Commerce, Von Achenbach, on the 2d of February, 1878, with reference to filling the position of chief of the institution to be founded:<sup>1</sup>

Seger belongs to the very small class of chemists who have acquired a good name by independent valuable work in the field of ceramics hitherto almost altogether neglected by science. Moreover, he understands in an uncommon degree how to get practical results from scientific investigations, and is, therefore, just the man for the place to be filled.

Thus Möller chose the right man, who alone was able to educate a school of younger chemists by his activity at this institution in the service of industry and manufacture.

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<sup>1</sup> According to documents kindly placed at my disposal by the Director of the Royal Porcelain Factory.

Seger, on his part, stipulated that he be permitted to continue the publication, together with Dr. Aron, of the *Thonindustrie-Zeitung* founded by them. If the main motive of this proviso was to be sought in the insufficient salary attached to the position, yet Seger in the correspondence that preceded his call correctly emphasizes the fact, in agreement with Möller, that

Nothing is so well fitted to keeping in close touch with the needs of the industry, as the publication of a technological journal of a wide circulation, and that such a connection is an indispensable prerequisite for the successful working of the Ceramic Experimental Institute.

It was also the desire of Seger to continue his lectures at the Royal Technological Institute in order to make the scientific results obtained useful to practice in the shortest way possible.

Under these auspices Seger was entrusted with the honorable office of head of the Chemical-Technical Experiment Station at the Royal Porcelain Factory on the 1st of April, 1878.

At the same time he laid down his duties as lecturer in the Royal Technological Institute, but kept the editorial direction of the *Thonindustrie-Zeitung*, while he entrusted the laboratory connected with it to his friend Aron.

It was quite in accordance with his agreeable character, that in his new position he won not only the devoted attachment of his younger coworkers, but also kept the approval and applause of the private industries, and gained the good will of his official superiors. The activity of the revered master in this period of his work is crowned with such brilliant successes as seldom fall to the lot of industrial chemists.

As has already been mentioned Seger spoke against the absolute value of the chemical gross analysis even before the introduction of the rational analysis; in the following years he set forth the undisputed value of the latter in a series of essays of widely differing content. He shows its importance for the explanation of the behavior of clays under heat, together with the ultimate analysis, in the essay "Concerning the Influence of the Essential Constituents of Clay on the Fusibility" (1878), and for the composition of bodies he discusses its value in the treatises "Investigation of Some Bodies for Fine White Ware" (1879), and "Concerning the Composition of some Foreign Bodies for Hard Porcelain" (1880). For the proportion of quartz, feldspar and clay substance it gives fixed points of support, and the empirical experiments with reference to the ratio to be selected between kaolin and plastic clay in the production of bodies are much simplified and their success insured, if the amount of quartz and feldspar in the bodies in question is kept constant and the proportion of kaolin or plastic clay is changed, carefully observing the respective amount of clay substance.

Extremely interesting is the essay, "Concerning the Relations between the Composition of the Sennewitz Kaolins and their Behavior in the Fire" (1879), in which Seger sets forth the strikingly different behavior with regard to shrinkage and porosity in the hottest fire to be attained in porcelain kilns, in fifteen different samples of Sennewitz kaolins after they had been washed as fine as is usual in factories. While the samples richer in feldspar produce white ware at this temperature or hard porcelain, if the feldspar exceeded 5 per cent, the trials low in feldspar show considerable porosity and a retention of their earthy character, so that we may assume that at this temperature there is no appreciable influence of the mineral components (quartz and clay substance) infusible at this temperature, and the small amounts of fluxes, feldspar, and iron compounds are not sufficient to bring about such an effect. It is clear that such properties of clays, so extraordinarily useful to technology, could hardly have been explained without separating the materials into clay substance, quartz and feldspar (the washing analysis fails more or less with materials washed to this degree of fineness), while with a knowledge of their composition according to definite combinations they become very prominent.

The essay already mentioned, "Concerning the Composition of Some Foreign Bodies for Hard Porcelain" (1880), which may be looked upon in part as the fruit of a journey of study undertaken at the request of the government in the year 1878 to Belgium and France, gave the direct impulse to Seger's greatest creation, the invention of the Seger porcelain named after him.

Among the porcelain bodies investigated were two Japanese bodies given to him by the Counsellor of Commerce, March, which with a strikingly small proportion of clay substance as compared with European porcelains showed a far greater plasticity than the continental porcelains richer in clay substance. This behavior suggested to Prof. Seger the introduction of plastic white ware clays for the production of porcelain bodies, low in clay substance and high in fluxes. With this was given the base for the Seger porcelain and all other soft porcelains patterned after it that consist only of quartz, feldspar and clay substance. The work that was undertaken by Seger for the investigation and reproduction of the technique and methods of decoration peculiar to Japanese porcelains produced a veritable flood of innovations in the field of porcelain, in a surprisingly short time.

From the report made by our dear master in the *Thonindustrie-Zeitung* at the occasion of the removal of the experiment station, from quarters occupied by it provisionally, to the building especially equipped for it on the 1st of October, 1881, the fellow ceramists know that the departed, in company with W. Timm, a thoroughly proven artist in the

ceramic field, had up to the year 1886 worked out the following decorative techniques:

For porcelain: Painting under the glaze in the glost fire; painting in gold and enamel on porcelain, glazed red in the glost fire; painting between two layers of glaze; painting in relief enamel over the porcelain glaze.

For white ware: Painting under the glaze; engobe painting on biscuit ware; painting with transparent pastes; enamel work in Deck's technique with colored glazes and solid outlines; painting with relief enamel.

This work had not merely an imitative character, but bears the stamp of the most independent originality; in the development of these techniques Seger replaced the lead glazes hitherto exclusively used in the production of white ware and in other branches of the clay industries by boric acid baryta glazes, free from lead; the transparent, relief-like lead enamel colors used on Japanese and Chinese porcelains were likewise replaced by such free from lead. The great master had not only succeeded in reproducing the technique up to that time peculiar to oriental porcelains such as the red-flamed suboxide of copper glazes, the green seladon glaze and the decoration with transparent relief enamels and in explaining their character, but also in producing an overabundance of new technical effects and new colors. I mention especially the introduction of the pink glaze and the egg-yellow uranium glaze for porcelain, the invention of an extended scale of hard fire under glaze colors, the development of painting between glazes for porcelain, in which the upper glaze is burned on as a muffle glaze at the melting-point of silver, the introduction of transparent and opaque enamels on porcelain in all shades; particular mention deserve the red suboxide of copper glazes shading off, at times, into blue and, at times, into green, and the painting with suboxide of copper colors under the glaze. The work executed in these techniques by Timm's artistic hand was shown first at the Christmas fair in the Berlin "Architekten Haus," in 1880, and later at an exposition given by the Austrian Industrial Museum in Vienna, in 1881.

A complete report concerning the manufacture of the Seger porcelain was made in the files of the *Thonindustrie-Zeitung* for the years 1891 and 1892 after Prof. Seger had resigned his office.

Just as he built up the composition of bodies according to entirely new views on the rational analysis, so also the way in which the great man deduces the colored glazes from the colorless, and the muffle glazes and enamels from the hard fire glaze by stoichiometric calculation from the molecular formula based on ingenious speculation and on exact reasoning, has wrought out new paths and new methods.

Concerning the techniques already mentioned for the decoration of

white ware we find exhaustive reports in the *Thonindustrie-Zeitung* for the year 1884; in this place it should be mentioned that the experiments with hard white ware bodies free from lime, patterned after those of Choisy-le-roi and English types were carried out. It would take too much time to review the results thus obtained; the industries have been able to make use of them and ceramists are familiar with results of these investigations. The researches concerning boric acid and baryta glazes were supplemented in 1889 by one on lime-alumina glazes which have become important for white ware, stoneware and a number of other products.

These brilliant successes did not fail to be recognized. After the death of his fellow student and friend, Dr. Hertzog, in 1883, who had but recently been appointed Director of the Royal Porcelain Factory on account of his successful activity as chemist of the institution, from 1866 to 1873, Seger was offered the position of director. However, since his time would have been completely occupied by the management of the institution, and he would have been compelled to put his chemical work into the background, he declined the offer of this honorable position. In April, 1885, he was honored by the bestowal of the title of Professor.

We have yet to mention the most popular work of the departed, concerning the composition of the "Standard Cones for the Measurement of Temperatures in the Kilns of the Ceramic Industries" (1886). These fusible cones which have been made accessible to the general industries, have in the course of years become an indispensable aid for the observation of the burning and the progress of temperature, as well as those mixtures serving for the determination of the refractoriness of clays, added to the former in 1888.

On the 1st of October, Seger, whose health had been seriously affected for some time by his restless activity, gave up the office of head of the Experiment Station to devote all his time to the periodical founded by him and the laboratory connected with it. There was likewise no lack of suggestive publications from the rich treasure of his knowledge at this time. Besides a series of essays on the production of the Seger porcelain (1891-1892) I mention his work on the composition of a biscuit body for soft porcelain (1892), on the production of roofing tile glazes (1892), and the patent on the manufacture of dinas bricks taken out in company with his collaborer, Cramer (1893). Ceramists owe to him also numerous apparatus; among others, a burette for the analysis of gases, a volumenometer, a down-draft trial kiln using illuminating gas as fuel, and the kiln using wood as a fuel for the burning of Seger porcelain.

He was incessantly active for the interests of the industry, in constant communication with fellow ceramists and always endeavoring in the most disinterested manner to serve his fellow men by lecturing in

the society and by instructing young technologists at the occasion of the annual courses in burning given by the society. What ever makes a scientist immortal fell to his lot, to open up to scientific investigation an industry built up only by experience and handicraft, which supports millions of people, which was nursed in its first beginning in hoary antiquity by untrained hands, which has become a criterion for the development of civilization of all nations, and which in our modern time has developed an artistic activity admired by the whole world.

He enjoyed general recognition, the fullest confidence and warmest love among his fellow ceramists. He was honorary member of the Union of the Ceramic Industries in Germany and honorary member of the Society of German Manufacturers of Refractory Products, and what he did as member of the council, as secretary for the "German Society for the Manufacture of Bricks, Clay Ware, Lime and Cement," in the way of devoted and sacrificing work will remain unforgotten in the hearts of those who have labored with him.

Hermann August Seger was a noble character. One needed only to look into his open, honest countenance to be convinced of the sincerity of his words, and to feel the kindliness of his manner; his departure has inflicted an unhealing wound in the hearts of those whose good star had brought them near to the departed. There was nothing equivocal behind his brow, and the features of his character were devotion to duty, modesty, and an unlimited willingness to serve. Thus he provided for his own family, thus he lived for friends and students, and thus he will live in the minds of us who knew him, honored him, loved him.

DR. H. HECHT.



## A. TREATISES OF A GENERAL SCIENTIFIC NATURE

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### The Process of Weathering of Crystalline Rocks and Its Influence on the Structure of Clay Bodies

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PROFESSOR CHAS. W. MESLOH, TRANSLATOR

The process of destruction to which the rocks which form the earth's crust are subjected by the never-ending activity of the water and atmospheric influences, causes at the same time the beginning of new formations. The material in constant motion through the activity of natural forces, forms a substance so fruitful for investigation and consideration, especially for the industries that busy themselves with the production of clay ware, that, although the same subject has been treated repeatedly in a thorough and scientific manner, it does not seem superfluous to review it, because an illumination from various sides may contribute still more to the understanding of the processes so important and so infinitely varied, and because only in this way is it possible to get an understanding of the peculiarities of a material as rich in varieties as clay is.

Nowhere, neither in organic nor inorganic nature do we find perfect rest ; matter is eternal, but the form in which it appears is subject to constant change ; the scarcely finished product falls a victim to the never-resting destructive agency of natural forces and in the continual change gives material for new forms. Even the firmest rocks, to which we are inclined to ascribe infinite duration, because they do not seem to undergo a noticeable change in the short time of human observation, cannot forever resist the leveling influence of water in union with oxygen, carbonic acid, and change of temperature, and are changed in form and substance or are completely destroyed and moved from their position.

By weathering we understand the process of destruction of a rock in which, through external chemical and physical influences, a part of the substance is removed, and thereby a lessening of the cohesion is brought about so that it is possible for mechanical forces to carry away the more or less changed residue from its former position and deposit it elsewhere to form new strata.

The diversity of chemical and physical properties of the masses subjected to change and of the destruction frequently modified by local circumstances causes such a wealth of forms to arise and offers such infinite difficulties to the consideration of the same from common points of view that the sciences engaged in these investigations have not yet succeeded in bringing into this chaos of peculiarities, rules and exceptions, that clearness which would permit the industries to use with confidence the scientific results and obtain from them the help which they so much need for their development.

On account of the generally considerable resistance, especially of crystalline rocks, and of the weak action of the forces entering into play, the weathering process occupies very long spaces of time and thereby makes difficult the study of the phases through which it runs in one and the same material, so that only by an extraordinarily large number of single observations a picture of the same may be obtained; and it is to this slowness of development as well as to the difference of the raw material and the kind of destruction that the extraordinary wealth of varieties of the product is to be ascribed. If in the case of a single mineral we consider the intermediate stages of decomposition with reference to its chemical character and physical condition this study affords, to be sure, a general view into the chemical properties as well as the structural relations of the product of decomposition, but furnishes such a changing picture that it seems almost impossible to refer the individual phenomena to the real causes and their effects because the process of destruction may take a different course in different places and at different times.

Not all constituents of crystalline rocks can, from their chemical nature, furnish clay on weathering, and probably in no

case do the clay-forming rocks find time and opportunity to undergo the process of decomposition to the last stage—to the formation of the still hypothetical pure clay substance—but they remain in the intermediate stage which more or less approximates the latter. Thus besides clay in the widest sense, there arise gravel and detritus, sand, rock-dust, loam, and loess, or if the process of weathering and destruction is interrupted and changes into the opposite process, the embedding and cementing of the smallest parts with or without the taking up of new substances, the original rocks may appear again in the form of conglomerates and breccias, sandstones and shales, perhaps also of crystalline rocks, with all possible gradations of chemical, mineralogical, and physical variations.

Of all the rocks which furnish the material for the formation of clay, only the group of feldspathic minerals or rather the rocks consisting chiefly of these, has been investigated thoroughly with regard to the process of weathering, while the decomposition phases of the minerals forming the chief materials for the origin of common clays, or of those which give to the common clays their peculiar character, and cause the specific differences as compared with the finer clays, are so much obscured that a more exhaustive explanation of these relations must be reserved for further very comprehensive investigation.

The results of the investigations of kaolins and plastic clays which we owe to the studies of Brogniart, Forchhammer, and Bischof, and which permit us to ascribe the origin of these finer materials to the decomposition of feldspar and the minerals related to it, do not justify us to infer the properties of those clay products which owe their formation to augitic, zeolitic and volcanically metamorphosed minerals, and although in the investigations concerning the decomposition which these substances undergo, valuable hints are given for future investigation, it cannot be denied, that at present that transparency of results has by far not been attained which the practical industries demand and science must at some time give.

If it is therefore impossible to determine definitely the chemical relations which exist between clay masses and the rocks

producing them, there is yet one factor, namely the parallel structure, which is common to all products of the decomposition of crystalline rocks. It claims the highest interest of the industries engaged in working them, whether it has advanced to a complete stratification, as with many sedimentary clays, or is noticeable only for short distances, as with kaolin.

A phenomenon which has the greatest significance for the inner structure of clay beds is, that all crystallized bodies show an unlike cohesion in various directions, and that this difference of inner structure is wont to show itself in a well-defined cleavage of crystals in a certain direction in a degree as much greater as the axes of the crystals differ in their relations.

Only with the crystals of the regular system is there a perfect equilibrium of the mutual attractive forces of the smallest particles, so that these show a cohesive force in three directions perpendicular to each other, while with all the others, that is the overwhelming majority of all crystalline bodies, the connection of the mass appears especially weak in one or two definite directions.

It is especially the influence of this difference of cohesion on the structure of clay beds to which I wish to call attention. In doing so I pass by the other qualities of clay, because this one, together with plasticity, is perhaps the only one, which appears common in a more or less degree and is so eminently able to increase the technical difficulties of clay working.

The feldspathic rocks of which we must assume that they, through the process of weathering, furnish the material for the formation of kaolins and plastic clays as well as an essential constituent of common clays and brick clay—the difficultly fusible part—show the phenomenon of unlike cleavage in a very striking manner and as soon as they contain considerable amounts of sodium and calcium are strongly subjected to the destructive influences of the atmosphere, so that the relations in question may best be observed in them.

The decomposition of the feldspathic constituents of crystalline rocks begins, as a rule, on the surface of the individual crystal and shows itself in a dimming of the crystal surface and a dull-

ness of the body. If we examine such a crystal in the first stage of weathering under the microscope, we see that it is traversed by numerous very fine cracks, more or less deep, which appear best defined in a direction parallel to the plane of the greatest cleavage. Through the influence of the water and the carbonic acid dissolved in it, some constituents, the alkalies, lime, silicic acid are carried away, and, assuming a pure potassium feldspar, the mineral would suffer a loss of about 53 per cent on complete transformation into clay. It is clear that with such a loss of substance, even at the beginning of the process of decomposition, either a diminution of the mass or a loosening of the structure must appear. Theoretical grounds as well as observation are opposed to the former. With a new arrangement of the smallest parts, which is accompanied by loss of cohesion, the breaks naturally take place in those directions in which the least mechanical resistance is to be overcome, that is in the direction of the planes of principal cleavage.

It is a phenomenon pervading all the processes of chemical affinity, that the degree of its action is very much influenced by the physical condition in which the active substances find themselves, and that also the conditions of cohesion produced by the difference of molecular attraction are of considerable importance. Substances which are vigorously attacked in a finely divided state or loose aggregation show a trifling, frequently altogether vanishing, energy in regard to entering into combinations with other substances when they pass over into a denser or crystalline condition; in a similar manner crystallized bodies are not attacked with the same force from all directions, but suffer destruction soonest from those sides, on which, on account of the inner structure, they show less density and cohesion. Since through the ready splitting of feldspathic rocks the easier chemical attack from one direction has already been indicated, and through the breaking up of the crystal into a number of thin plates the entrance and the destructive effects of the water is especially favored in the same direction, it is clear that the weathering must have the mechanical effect of breaking up the minerals into laminae, becoming thinner and thinner, which

finally reach the degree of great fineness as the glittering mineral fragments of rock flour will frequently show.

The influence which this more rapid progress of the process of decomposition exercises in a definite direction on the structural relations of the product of weathering, unless at the same time a removal of the masses weakened in their cohesion has taken place, is less striking than where at the same time there has been a change in location. The products of decomposition, still found in their original position, yet show the structure of the rock out of which they have come forth, even though somewhat distorted by the loss of substance and volume. In most cases, especially then, when not all the feldspathic substance has passed over into an amorphous clay mass, there still appears in the latter a cleavage corresponding to the original crystalline structure produced by parallel feldspathic remnants ; this parallelism, however, does not extend beyond the limits of the original individual crystals and in the case of previously very fine-grained crystalline texture may vanish altogether from our observation, and will never be able to impress upon the forming clay mass a stratified or slaty character if the individual crystals were not already in a parallel stratified position before.

The structural relations of the clay must, however, become much different, if, besides the weathering, a washing has taken place. The horizontal parallel structure of sedimentary clay beds is caused by the presence of layers which are chemically and physically different from others near by, so that in different heights of the deposit, sand, rock flour, or clay predominates, which themselves are again different with reference to grain, permeability to water, and plasticity on the one hand, and on the other hand show differences in the mineral detritus, the crystalline residue appearing in extremely thin laminae in which the weathering process has not progressed to the complete extraction of the alkalies and the loss of crystalline texture connected with it.

A small fragment of rock, transported by water, with attendant mechanical grinding, which, entirely neglecting its mineralogical character, we are wont to call a grain of sand, when of a certain size, will in general possess a spheroidal or poly-

hedral form and when placed upon a horizontal surface will find itself in stable equilibrium in the most varying positions ; quite different is it, however, with the crystalline fragments broken up by a chemical process to extremely thin flakes, which, carried away in company with the amorphous mass of clay and transported gently on account of their lightness, could escape destruction by rolling and grinding. Where these laminae are deposited at the same time with the clay they could only be in a position parallel to the surface of a sediment, that is horizontal, because with them there is only one top and bottom side and they could find support in no other position. The consequence of this is, that the parallel structure formerly belonging to the individual crystals but not to the crystalline rock as a whole, has now been transferred to the whole sedimentary deposit in a greater or less degree whether this deposit be clay, or on account of later metamorphosis, shale, slate, or mica schist, and is influenced more or less by the fragments of rock, rounded and bound to no definite position and mechanically broken, and amorphous clay masses.

The presence of these infinitely thin and dust-like mineral remains with their corporeity, aiming for a definite structure of the clay masses, may be followed with the help of a microscope through all varieties of the same. The weakening of the cohesion, however, and diminishing of the plasticity so disturbing in the industries appears in a much less degree with the kaolins in their original beds and with the unstratified plastic clays than with the sedimentary clays, loam and marl deposits.

It seems striking, in view of the apparent importance of the physical condition, that in the majority of investigations which we have concerning clays so little attention has been given to this, and that no regard has been had for the chemical difference of the constituents often visible to the naked eye, but that in a one-sided way all was thrown into one pot ; or, if a separation of sand, rock flour and clay was attempted, the investigator, except in a few cases, was satisfied with the determination of the mutual relations by weight without looking more closely at the peculiarities of the various components.

When, in former years, we were again and again urged in

the works of Tuerrschniedt, published in the *Notizblatt*, to investigate the properties of clay in all directions, especially on the physical side, an urgent admonition may not seem superfluous in view of the deficient knowledge which we have concerning the peculiarities of this important material; science finds itself in rather a helpless condition in the face of the demands that practice makes upon it, not so much because the points of view from which it must work for the end are not sufficiently fixed, but because that method has been wanting which furnishes results of real practical use for the ceramic industries.

Clayey masses serving for the manufacture of glass and cement in which their character has been utterly destroyed, require a determination of their physical properties in a much less degree than the clays intended for the production of clay wares; indeed, we can say that the *en bloc* analyses, as they have heretofore been carried out and judged in practice are of no value for the clay industries if a more dignified place is not given to the mechanical analysis by means of the washing apparatus and microscope side by side with the chemical analysis; only then, when this gap in the older and imperfect examinations has been filled out, or a sufficient number of new ones, having more regard for the physical side, have been fixed for the examination of the qualities in question, can those conclusions be drawn from the scientific results which, as in other branches of technology, will wrest from crude practice that respect for science which it needs for mutual cooperation.

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### Crystallization and Its Significance for the Clay Industries

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PROF. CHAS. W. MESLOH, TRANSLATOR

The demands which the cement and the ceramic industries make on the qualities of clay are as different as the purposes which these industries pursue.

In the manufacture of Portland cement we have in mind

the obtaining of a product of a definite chemical composition, and since the character of clay as such must completely vanish in this, the mutual relation of the individual constituents is to be considered above all things, and the physical condition in which these are found must be considered only as far as it opposes greater or less difficulties to the destruction of the clayey character.

The clay industries, on the other hand, pursue a quite different purpose in the treatment of their raw material. The limits within which the chemical constitution of clay may vary are very wide and, since the clayey character of the material is to be preserved, its physical qualities and those of its essential and accessory constituents are to be placed in the foreground. While for such a purpose the chemical composition of clay, as a whole, appears more indifferent and accidental, inasmuch as it depends on the mutual relation of clay, rock flour, sand, accidental admixtures and their chemical constitution, the *physical* properties of the same, the grain and its form, capillarity, plasticity, fusibility, etc., are of greater importance, and the chemical constitution of each one of these constituents is to be considered only as far as it permits us to infer the physical properties of the whole. It is surely a serious mistake to treat materials so heterogeneous, chemically and mechanically, as the clays and earths used in the ceramic industries like substances chemically and physically homogeneous, as for example glass, and to base conclusions with regard to their properties on their chemical composition.

The chemical changes, which the materials of the ceramic industries suffer in the course of manufacture, step into the background, with the exception of the loss of chemically bound water, which has as a consequence the loss of plasticity, and must not be produced in the same degree as in the manufacture of cement and glass or the material will lose its earthy character. In fact it seems advisable to drop the investigation of the chemical composition of clay as a whole and put in its place a deeper study of the composition of the essential and accidental constituents, in order to infer the properties of the whole from the properties of the components thus obtained. For example, we need

not ask how much pure clay and silicic acid we have in clay, but what part of the clay and silicic acid belongs to the sandy constituent of the clay, what part to the silty, or the clayey constituent, and what physical properties must we, according to these data, ascribe to the sand, rock dust, clay, etc., individually.

Just as important an influence on the physical properties of clay as the chief constituents of the same, have the accidental accessory admixtures, since these are more easily subject to changes and change of place within the clay mass than the former, chemically more indifferent, whereby changes are produced in the clay which have, as a consequence, qualities undesirable in its manufacture.

In stating that in the consideration of clayey masses from a ceramic standpoint the physical properties of the whole are to be placed in the foreground and that the chemical properties do not justify us in drawing conclusions, but only are of value when one resolves the heterogeneous mass into its elements and tries to determine their chemical qualities, and basing on this, also their physical properties, a method is indicated which demands a far more complicated process of investigation than has so far been used, but on the other hand justifies us in drawing conclusions reaching farther than the *en bloc* analyses heretofore chiefly used for technical purposes. If in some cases a separation and a separate analysis of the pure clay substance had been made and the other constituents not considered, this is justified, where it is a question of a purely scientific speculation directed to one point, whereas in the treatment of the material for technical purposes the determination of the properties of the other, sometimes predominant non-clayey constituents, is just as much justified as that of the clay substance.

It can not be denied that in the examinations of clays scrupulously accurate analyses of the material have heretofore been made but that little has been learned concerning structure, condition of plasticity, power of absorbing water, shrinking on drying and burning, form and size of the grains of sand and rock dust, concerning the peculiarities of the concretions, concerning

efflorescences and incrustations, and in stating that in the consideration of the properties of clay for the purposes of the clay industries we must put ourselves more upon a physical than a chemical standpoint, permit me to consider more in detail the effects of the force which has the greatest influence on the properties of clay and the wares produced from it, which, as no other, working mysteriously and in secret, can slowly but surely bring about the greatest changes and destruction. I mean the power with which the smallest particles of similar matter strive to arrange themselves into geometrically limited bodies: the power of crystallization. We shall have to consider its influence from various points of view, namely:

1. With regard to the structure of the raw materials.
2. With regard to the capability of further weathering, and the fusibility of the clay.
3. With regard to the destruction of the products of the clay industries through this force.

## I

If through a large number of investigations and by numerous observations of the weathering of crystalline rocks it seems proved that the extended and exceedingly varied group of rock forms which we know as clay, shale and slate owe their origin to a chemical decomposition, mechanical splitting and breaking up by friction and grinding, the thought arises whether the inverse process, as chemical science offers it more frequently, regeneration can not take place by a transposition of the individual constituents to new combinations, and the taking up of substances lost in the weathering by new infiltrations.

We are led to this speculation by the structure of some kinds of porphyry which cannot hide the character of a rock formation formed by sedimentation, as well as by gneiss and mica which show a most pronounced cleavage, also by the transitions which we find in many places from clay through slate and mica to pronounced crystalline feldspathic rocks.

If we consider all these formations without regard to their chemical constitution, keeping in mind only their physical state,

we see an uninterrupted series of the same peculiarities in a varying degree, which tempts us to ascribe a common origin to all these products and to ascribe their difference only to the degree and the time of the action of those forces which have impressed changes upon all of them without destroying their character altogether. Just as in the case of the weathering process we can follow an uninterrupted scale from crystalline rocks, disturbed in their cohesion by coarse detritus, sand and clay, so also by an inverse metamorphosis and infiltration we can pass from the detritus again to the solid rocks, the slates, sandstones, conglomerates and breccias up to forms with a pronounced crystalline structure.

Even if nature does not grant to the human eye a look into her most secret workshops, if she does not show how she changes clay into shale, sand into sandstone and wacke, or forms a crystalline lime or marble out of the deposits of calcareous shells, if she has not yet, up to this time, permitted us to determine the conditions under which, in heaps of detritus formed by friction and weathering, the like constituents move to certain centers of concentration and become new crystalline formations, speculative science, by a comparison of the products upon which these unknown influences have worked for an unlike duration of time or with unequal intensity, yet furnishes a hold as to how these may have originated and brings us closer to the workshop of nature, for the most part not accessible for direct observation.

We have not yet succeeded in seeing in nature those bodies which in ordinary life seem insoluble in liquids arise and grow as crystals, yet they may be observed as accomplished facts in every rock, and by their being found in company with others, by their position and structure they show that the formations must have taken place under different circumstances than science has attained in some happy artificial imitations, because the processes of nature take place more slowly than do scientific investigations in which more powerful agencies must be employed because human observation is limited to a short space of time for the observation of natural processes.

As has been stated, science is not yet in position to deter-

mine beforehand and explain sufficiently the conditions under which formations in the surface of the earth can assume another form. What appears to have been explained rests in part on a blind belief in authority which retards true investigation, or it is a structure of speculations based on an insufficient number of observations, which to-day or to-morrow can break down under the force of new facts. I do not deem this the place to discuss the scientific quarrels concerning the origin and change of rocks and to weigh the pros and cons of the various views, but to discuss rather matters of practical interest in speaking of the changes in the substance of clay masses and the influence which these may have on the physical properties, and if I am obliged to consider some times other allied rock formations it is only because certain peculiarities of clay are seen in them in a more striking way.

If in the previous essay the influence was set forth which the crystalline condition of a rock has on the structure of the clay arising from it by weathering and removal, we have only arrived at the regular, horizontally stratified deposits whose occurrence in nature forms the exception; the other structural relations, the concretions, etc., find no explanation in it.

It is a peculiar force varying very much in its intensity in various compounds, which so works upon the smallest particles of matter, that especially then, when the state of the molecule has a certain freedom of motion, that is, in the liquid or gaseous state, on passing into the solid state similar elements assume such a position in regard to one another that bodies arise which are bounded by plane surfaces, intersecting each other at constant angles, and that the tendency to deposit themselves on a similar substance and therefore to form as large crystals as possible is in many cases so great that through the act of crystal formation forces are produced which are often enormous. The attractive force of the smallest particle of a crystallizing body which gives rise to the formation of the crystal finds a constant resistance within the surrounding medium in the firmness of the latter and if the effects of the molecular attraction on the medium are not always the same it has its reason in this, that the former as well

as the firmness of the latter may vary between the widest limits, according to the properties of the materials in question and the circumstances which happen to prevail.

It is probably not superfluous to mention that the essence of a crystalline condition is not to be sought in the development of a mathematical boundary as much as in the presence of the structure of the mass which stands in a certain relation to the external boundary and shows itself in the most cases in a cleavage in one or more directions, which is quite constant in crystals of the same substance and form. A body which is limited by plane surfaces is for this reason by no means a crystal, but only becomes one when the external boundary appears as the expression of the internal structure; on the other hand, the great mass of minerals occurring in nature, with the exception of comparatively rare and therefore all the more admired cabinet specimens, do not show the bright surfaces so striking in these but may nevertheless be crystallized, if the crystalline arrangement and its consequent peculiarities show it, though the external surfaces could not be developed for the most part on account of lack of space.

It can therefore not seem strange to us, when in the appearance of crystalline substances nothing is to be observed of the mathematical bounding planes, while the substance in other respects shows all the peculiarities of the crystalline conditions.

As stated above, the formation of a crystalline substance presupposes a certain freedom of motion of the molecules to deposit themselves side by side according to definite systems, and where this is wanting and all constituents are in the solid state an external mechanical influence will be necessary, as we can observe in the crystallization of railroad car axles in consequence of long continued blows.

In general we can, however, say that for the formation of crystals at least one solvent must be present for one or several constituents of a crystal-forming body, to bring about the condition of freedom of molecular motion, and in fact the crystals occurring in nature with the exception of the real volcanic products, in which other circumstances play a part, may be referred

to the influence of a solvent. The liquid working in the above-mentioned manner in the natural phenomena can hardly be any other than water, whose dissolving force is mostly increased by dissolved carbonic acid, oxygen, organic substances, salts and a higher temperature.

We shall hereafter consider chiefly the influence of water as the cause of changes in the clay and observe the effects which it may exert on the structural relations of the clay.

It is a fact long known, that dissolved salts, even when they are present in small quantities, can bring about the cementation of bodies to solid masses, quite insoluble in the same solvent, whereas with the absence of the former they dry up to an incoherent mass. Slate and the forms related to it are generally considered as having arisen from clay deposits by hardening, and this hardening has in most cases been brought about by the interdeposition of a feldspathic mass which has in part changed the original clay substance, in part simply cemented it. How this cementing substance got into the clay deposits or was formed from its constituent parts is a question which has caused a violent polemic in the geological world, which seems, however, to be decided in favor of those who see in it an effect of water, perhaps with the cooperation of an increased temperature, while the defenders of the purely igneous metamorphosis begin to find their position desperate.

In the consideration of the structure of clayey deposits we are struck not only by a separation in a horizontal direction that shows itself at a first glance as the consequence of sedimentation, but we find yet other phenomena, which teach us that after the deposit was made changes have taken place in the material; these changes may be divided into such as have been called forth by purely chemical effects through the agency of water and into mechanical changes which in most cases find their first cause in a chemical process.

After the completion of the weathering and washing process, which the original rocks, from which clay has been derived undergo, the chemical effect of the water and atmospheric agencies does not cease, but exercises its influence still farther according

to circumstances. A further weathering or lixiviation takes place, or certain substances are dissolved and deposited elsewhere or on a similar substance, that is a wandering, as it were, of single constituents takes place within the clay mass or there is an introduction and fixing of substances not before belonging to the clay substance.

In all these cases water plays a very essential part as the vehicle, but the success of its effects, as we shall see farther on, is chiefly caused by the circumstance that in its circulation a definite direction is prescribed to it by the manner of the origin of the clay bed. Clay in its moist condition in the earth maintains itself impervious to water in a direction perpendicular to the stratification as no other formation does and permits the circulation of water only between the dividing planes of its strata and in the channels which have been caused by the interdeposition of foreign, especially vegetable, substances and in the crevices caused by crushing.

This effect of water, limited in one direction, appears as of the greatest importance for the changes taking place in the clay mass, in so far as a definite direction is again given by the one-sided circulation of the water to the decomposition, new formations, and concretions taking place in it.

We know from the measurable fillings in cracks and hollow spaces of solid rocks, that the substances deposited there, according to their nature, show such a structure that they may be scaled in a direction parallel to the edges more easily than in other directions, or that they show a cleavage which forms a definite angle to the passage way. The latter case is true, for the most part, when the substance filling the passage way is in a crystalline condition and has its cause in this, that with the one-sided direction of the liquid causing crystallization, the individual crystals formed have taken a similar position in regard to it.

If we extend this experience to the process of hardening of clay to slate, whether this was caused by the introduction of new substances by the penetrating water, or that the constituents of the cementing substance were taken from the clay mass

itself, then, since we must assume the water circulation in parallel but infinitely fine crevices lying very near together, the stratification will appear still more prominently with a deposition of the cement in a horizontal direction and passes over into a true slatification, whereas, with an arrangement of the cementing substance at a certain angle, the original stratification can be weakened or vanish altogether while in its place there appears a secondary or so-called false slatification.

Daubrée first attempted an explanation of the preservation, dislocation and secondary slatifications in sedimentary layers and thought this ought to be ascribed to the effect of the mechanical pressure produced by the weight of the sometimes very thick layers and the rock masses lying upon them.

This view has certainly its justification, as we always see, that when the peculiarities of cohesion of a compressed body allow a change in form, even though slight, by mechanical pressure, a parallel structure will be formed which runs parallel to the pressing surface. We see this structure, for example, in the case of iron when it is rolled or drawn, where after etching with an acid a characteristic arrangement of the mass always appears; in rolled plates this arrangement is laminar, in drawn wires it is fibrous, which at once shows itself as the effect of the pressure.

This explanation, however, does not suffice for all cases, especially does it not show how this external pressure could transmit itself so equally in a fixed rock formation, that the direction and intensity of the dislocations and false slatifications can remain constant, while in other phenomena of this kind we notice the effect of the pressure pronounced in the neighborhood of the surface, with a rapid diminution toward the interior. We can note this assumption in rapid progression even in soft clay which has been exposed to a one-sided pressure on the potter's wheel. If we observe with a magnifying glass the broken edge of a sherd of a turned vessel we find that through the manipulation, a parallel structure has been formed in it, that the grains of sand and rock flour have taken such a position under the pressure of the hand that their longest dimensions are arranged in the direction of the movement and the pressure, that

is, parallel to the inner and outer side of the sherd, that this structure, however, loses its intensity a few millimeters from the surface and cannot be noted at all in the center of a somewhat thick sherd. In the natural occurrences, however, we must mark yet another process which can exert a pressure on the hardening clay masses and this lies in the process of hardening itself, in the pressure which the cementing substance exerts on the inclosing medium during the process of crystallization.

There are enough examples known that show with what force crystallizable substances attract other substances like them, strive to deposit them on their surface with an enlargement of the individual crystals and procure for themselves the necessary space by crowding out other substances or taking them up mechanically within their laminae. The pressure exerted by the formation of crystals is so powerful and so continuous that it can not well be imagined in any other way, so that it could be looked upon properly and with great probability as the only or at least the most frequent cause of the elevation of the mountains.

That such an exertion of force, if it takes place in the interior of a clay mass, can not remain without a far-reaching influence on the structure of the same is clear, and if to this is added the circumstance that to the pressure produced by the interdeposition of the crystalline cement a definite direction is given by the one-sided circulation of the vehicle causing the formation of the crystal, that is of the water with the substances dissolved in it, it cannot seem strange to us if the effect in the same layers remains the same, often with astonishing constancy. Since the structure forming pressure is exerted by the crystalline surfaces of the infinitely small crystalline particles causing cementing, the cleavage of the same, however, does not stand in quite so simple a relation to the external boundary surfaces. We will not be able, as a rule, to form a conclusion as to the nature of the cement from the direction of the structure produced by it, but only see from which side the greatest pressure was exerted in the formation of the crystals.

In clayey deposits and related formations there are frequently found concretions which are strikingly distinguished from the

rest of the mass by color and structure, hardness and plasticity and are of the greatest importance to a clay because they oppose considerable difficulties in obtaining the homogeneity absolutely necessary for clay products of every kind as far as this is possible from the nature of the material. The most varied explanations have been attempted of the origin and nature of these occurrences, concretions and clay balls, but no solution is altogether satisfactory. Surely not all phenomena of this nature can be placed under one head, since the structures are of the most varying kind, now concentrically laminar, now plane, now breaking up in cleavage planes at a constant angle to each other, now without any prominent stratification, traversed by veins of calcium and iron oxide. Some have thought that these formations ought to be looked upon as subsequent products of weathering, in part as products of the evaporation and contraction within the clay bed, in part as new formations or beginnings of the origin of feldspathic crystals.

That these concretions are not always secondary products of the weathering of feldspathic rocks is shown even by their external appearance. They possess the property of the clay to bind a certain quantity of water by surface attraction and to offer a certain resistance to taking up of more water, that is, of being impervious to water, frequently in a far higher degree than the surrounding clay mass; moreover, they often show themselves more plastic than these and require very careful manipulation in order to embody them in the rest of the clay mass to the acquisition of a certain homogeneity. These concretions would not show these phenomena if they were a product of subsequent weathering or were still in the stage of weathering, because we know that feldspar in its change into clay loses 55 per cent of its weight or 33 per cent of its volume; moreover, the product is all the more plastic the farther the weathering has progressed. A hollow space would therefore have to arise, offering room for other deposits, or the mass would have to be in a less dense state than we observe it, for under these circumstances there is no cause for condensation.

To assume drying out of clay beds and ascribe to it the

condensation and greater resistance of certain particles seems even less admissible than weathering. According to the nature of clay, evaporation can take place only on the surface; the clay, then, in consequence of contraction breaks up into pieces sometimes quite regular which look very much like fragments of crystals, but from their character cannot be compared with them at all; moreover, how some parts of the clay bed should be so much favored as to be able to give off water by evaporation while surrounded on all sides by a moist substance and perhaps themselves containing passage-ways for water in the form of roots, veins of iron and lime in their interior, cannot be imagined.

The deposits in clay called concretions or balls are from their nature always condensations of the mass, and such condensations can only be explained by a mechanical pressure either from without, or by the penetration of foreign substances and increase of substance and consequent pressure from within, and within a certain space, which may be accompanied by a simple cementation.

To determine of what kind these deposits and transformations within the clay are, and the changes produced by them, we altogether lack, on the one hand, positive and comparative observations; on the other hand, it is so difficult to examine them from fixed points of view on account of the variety of the material and the circumstances which give rise to the changes that I must limit myself to illustrating the phenomena of this kind by a few examples.

If organic remains, for example roots, leaves and lower plants, bodies of animals, etc., are embedded in clay they form an extraordinarily favorable territory for the migration of single constituents of clay, not only because they favor a stronger circulation of water in such places, but also because they furnish the material for the formation of carbonic acid which strongly supports the action of water. If now, as is nearly always the case, the clay contains compounds of iron these so act upon the carbonaceous substance that they gradually destroy the organic material and are dissolved in the carbonic acid formed from it in the form of a ferrous bicarbonate, and in this form are easily

carried away, following the direction of the circulation of the water. This ferrous carbonate is a compound very easily decomposed, and changes again into what it was before, generally ferric hydrate, if it can give off its carbonic acid to a body which shows a greater affinity for it, for instance lime, as soon as it is removed from the sphere of activity of the organic substance, and instead dissolves a quantity of lime corresponding to the amount of carbonic acid lost, which then continues the migration until also it finds an opportunity of depositing in an insoluble form. Where now these deposits of iron or calcium oxide find a resting place after their removal and fixing, they change and cement the clay, and after having been introduced at one place, perhaps in fine veins, they come out again at another in the form of argillaceous iron ore, septaria or balls of marl, or as veins of iron and marl. The peculiarities of form, hardness and chemical composition which such layers of clay undergo by such a change of place of single substances are always dependent on their chemical and physical condition and consequently show the greatest variation. The concretions which arise from the local deposition of iron oxide and generally also carbonate of lime taken from other parts of the bed probably rarely have an effect that changes the structure because they are nearly always separated out in a non-crystalline condition, and only cement the clay substance in the proportion as it affords a passage-way for the liquids bringing about the change of place, to cylindrical or spheroidal masses with a shell-like structure of a cylindrical or spherical form or they form a filling, hardening, or dendritic incrustation in veins, cracks and on planes of faults.

Of a different effect on the structure than these cementing deposits are the crystalline deposits in the clay inasmuch as besides the cementing they produce a condensation of the material hemming the formation of the crystal on account of the pressure exerted by the mutual attractive force of its smallest particles, without necessarily causing a great change in the chemical composition of the clay. Gypsum may serve as the most common example of this kind. Gypsum may be introduced partly from without by water penetrating into the clay, in part it de-

velops in the deposit itself by the mutual action of carbonate of lime, iron pyrites and oxygen, and shows a tendency, like a few other accessory constituents of clay, to deposit in large crystals, a property which is especially favored by its comparatively great solubility in water. Gypsum is a very common constituent of clay and appears in it in, for the most part, clear colorless crystals frequently of considerable size, which are embedded singly in the clay mass or seem to have grown together into star-shaped or spherical groups, frequently on balls of marl, which have given a part of the material for their formation; where now the conditions within the clay bed are favorable for the formation of gypsum, fresh crystals will develop in larger or smaller specimens and wherever the necessary space is wanting will procure it by a crowding and compression of the clay mass.

But the effects of crystal formation do not always appear in this simple way; the phenomena of structure show that sometimes the cementing and direction giving crystalline deposits do not appear in connected individuals, but as we have already seen in the case of hardening of slate, lie scattered within the clay mass in the form of extremely fine lamellae and give to it a certain cleavage at constant angles.

Some observers have believed themselves justified in seeing in some condensations of the clay mass beginnings of feldspar formations and have supported this assumption by the observation that the angles of the cleavage planes of the clay were very similar to those of the feldspar crystals; however, in the first place the measurements of the angles of the so-called clay crystals show a greater deviation from the normal angles of feldspar than the limits within which the angles of feldspar of various places and composition vary; in the second place even an agreement would not justify the assumption that a feldspar formation had begun, because the cleavage appearing as a consequence of the interdeposition cannot be looked upon as the expression of the cleavage planes of the material causing the pressure, but as that of the direction of the rapidly growing surfaces hindered in their development by the enclosing material.

In some cases, namely, when the principal planes of cleav-

age of a cementing body agree with the planes of the external boundary, such a separation may take place, that one can easily recognize the cementing material, so for instance in the case of the crystallized sand of Fontainebleau which is impregnated with calc spar and only in consequence of this shows a cleavage according to the rhombohedral surfaces peculiar to calc spar.

The separation of marl in the shape of salt crystals, which has been observed by Camillus, in America, according to Beck, I think, ought to be placed into this class. There is a layer of marl, several feet thick, which consists of crystal-like concretions of marl, in the shape of cubes, grouped to form the hollow pyramids, observed in salt. The crystal groups are one to eight inches in diameter and their independent formation in a solution of salt, without sinking before they attained this enormous size, seems improbable in these formations.

I will mention yet another example of this kind which seems interesting, because it has developed only a decade ago, in which to be sure, the clay was given its form by a salt which shows a tendency to crystallize as perhaps no other.

In a Rhenish alum works crystallizing vats had been made of sandstone plates sunk into the ground and tamped below and on the sides with a very unctuous clay to preserve them impervious to the liquor. After some years the sandstone had so weathered through the action of the liquor that penetrated into its interior that they had to be removed. The surrounding clay formerly impervious to water had undergone a most remarkable change; to the depth of from a half foot to a foot it had completely lost its character and had changed into a loose aggregation of octahedral crystals from a quarter to three-quarters of an inch in size which enclosed between them a small amount of clay substance. These fragments were very easily broken and consisted of pieces of clay which were traversed by a large number of lamellae of alum and frequently contained a skeleton of alum which gave to the clay mass its external form while it itself had no connection with the crystal-like form developed. The mechanical effects which were produced by this

crystallization were no less noticeable. The side and partition walls of the individual liquor vats were raised and broken, and that part of the building in whose cellar the plant was, had been so raised by the penetration of alum liquor into the foundation that it suffered a break and dislocation of about two and one-half inches from the openings of the door and windows to the ridge.

That, moreover, a formation of crystalline silicates may take place in detritus without our being able to indicate definitely the conditions under which such processes can occur is shown by the frequent occurrences of such in sedimentary layers, the occurrence of mica in kaolin and sandstone, of feldspar in slate, of sanidin in the trachyte conglomerate of Langenberg and Lutterbach in western Prussia. Jenzsch describes crystals of sanidin, a variety of feldspar, of one and five-tenths millimeters length, which are found in the clays of Tannhof and Buschberg near Zwickau, formed from the melaphyr. Their surfaces are usually somewhat rough and covered with a second coat of the surrounding clay. They are clear as water and possess a lively luster which may be especially noted on the cleavage planes. Since the melaphyrs of that place do not contain sanidin as a component, these crystals must have originated in the clay itself during or after the process of weathering, as well as the black scales of mica that are found with them.

## II

It is a peculiar arrangement in the laws of nature that the effects which are produced by them may be referred to a very few forces and that the same force may serve to annul an effect which it itself has produced. We see this plainly in the processes and manipulations to which clay and the related formations must be subjected in order to produce from it artificial imitations of natural products,—solid rocks,—the aim of all ceramic industries. According to the fundamental laws of mechanics the effect of a force can only be annulled by an equal force working in an opposite direction. The working of clay requires a mass whose smallest particles may be more easily moved than

is the case in the natural occurrence, not only to give to the more plastic mass a definite form with greater ease, but also to destroy the inequalities of the mixture as they are produced by the formation of the material through the separation of like substances in the washing process, through the differences in specific gravity, and according to the deposition of like parts of matter by molecular cohesion.

The attractive force between clay and clay, and water and clay which gives to our material a certain firmness in its moist condition, causes a certain resistance to the taking up of more water, which is increased by the approaching of the molecules due to mechanical pressure, whether the pressure be exerted from without or arises from the interior itself by a migration of component parts, must always be broken before artificial products can be produced and the ways of accomplishing this depend, first, on the nature of the raw material, and, second, on the amount of manipulation which must be given to it.

If the condition of the clay and the purpose pursued in its employment is such that solid deposits, which cannot be reached through water, must first be removed from it, an artificial separation of such disturbing substances must take place, and in this case washing is in order ; but if from the nature of the material such a separation may be dispensed with, at least a loosening of the structure is necessary in order to give to water uniform access to the interior, also to allow the water to take part in bringing about the greatest homogeneity of the mass. The uniform introduction of water by simple softening and subsequent mechanical manipulation proves, for the most part insufficient, unless the latter has been performed with the greatest care, and some means must be employed to break the resistance which clay offers to the taking up of water ; these are either drying or freezing of the clay.

Air-dried clay behaves very differently toward the influence of water from that which has already fixed a certain quantity of water by surface attraction ; while the latter opposes the greatest resistance to the taking up of water and can remain in contact with water for weeks and months without essentially in-

creasing the amount of combined water, the former absorbs it with the greatest eagerness, and causes a very sudden increase in volume, which divides the dried mass by numerous cracks into small parts that permit an easy and uniform passage of water. This kind of treatment must be considered an exceptional one for factories, since, in regard to cheapness, it is far inferior to the method of weathering, or better, wintering. Here again we meet an effect of water at the moment when it passes from the liquid to the solid crystalline state and it will repay us to consider somewhat more closely the events taking place.

Compared with all other liquids, water shows the anomaly that it does not suffer an increase in volume by an increase in heat, and a diminution of volume by a decrease in heat according to a rising or falling scale, but reaches the minimum of its volume at a temperature of  $4^{\circ}$  C., expands again on a further decrease in temperature, slowly at first but very suddenly and intensely on going over into the solid condition so that even, by the mechanical effect produced, considerable manifestations of force, loosening and breaking up, may be caused by this peculiarity in a mass soaked with water. The effects of freezing water would, however, not be as intense by far, if they were not supported by another factor, shown by the water in its passage into ice, a great tendency to assume a crystalline arrangement and all the peculiarities that we know in crystalline substances. We can easily observe the influence that is exerted by the crystalline form of water on its change into ice in every piece of clay, for instance, an unburnt and undried brick which is exposed to a low temperature. In such a piece of clay we see cracks with the naked eye and, still better, with the help of a magnifying glass, which have the flower-like form peculiar to crystals of ice, and change the piece of clay into an aggregation of loosely connected clay splinters. This breaking up is not caused by the expansion which accompanies the change of water into ice, for in this case a uniform expansion would take place, and in consequence of this a break could take place only at the places weakened by the lack of homogeneity, but by the fact that the water was attracted and deposited in the solid state where it

already found a beginning of the formation of ice crystals, that the crystals of ice forcibly procured the space necessary for their development by shoving aside the clay, and thus brought about not only an increase in volume and loosening of the mass, but also produced a network of fine channels after the disappearance of the ice which permit the atmospheric influences to extend their effects far into the interior.

The benevolent influence which the freezing process exerts in breaking up the mass of clay has always been sufficiently appreciated by the industries, and it seems superfluous to recommend it, even though scruples have been raised against it that were based more on opinions than on positive scientific reasons. If in many cases those results have not been obtained which were expected of it the reason for it is found in the fact, that the process was not fully understood and the necessary arrangements were not made. If, for instance, one makes piles of clay in autumn, 10 to 15 feet high, and expects it to be broken up, he may be convinced in spring that only a very small part has experienced a breaking up, namely the external part affected by the rain, snow, and frost, while the rest is in the same condition in which it was deposited in autumn; the labor and expense might therefore have been saved. If one desires an effective result from the freezing process, it is very essential to make the layers of clay to be wintered no deeper than the frost is wont to penetrate into the earth and to pile it up as loosely as possible so that the water for the formation of the ice may be introduced in an abundant amount as deep as possible by the penetration of the atmospheric precipitates.

Some clays, especially those very rich in pyrites, which are not rare as companions of the alum deposits in the beds of lignite, have the property of weathering, exfoliating and breaking up into small fragments in a very short time after coming in contact with the air. The cause is here essentially the same we have learned to know in the freezing of clay; through the influence of the air, crystallizable salts are produced, chiefly sulphate of iron, sulphate of magnesium, sulphate of aluminum and gypsum, which not only assume a greater volume by the chem-

ical union with water but also produce a breaking up of the solid mass of clay by the force of crystallization, by the concentration of the scattered material to single points for the formation of larger crystals in the same manner as we have learned to know it as the effect of frost.

In the transformation of clay to solid bodies, no longer capable of being softened by water, we again meet the influence which the crystalline condition of some constituents of the same exercises on its qualities, to be shown in a manner completely different from the effects heretofore described. I should not like to pass this over in silence because it seems as though it had not been appreciated in ceramic literature as it deserves; I mean the influence of the temperature which is necessary for the attainment of the matured condition of the burned clay.

By the condition of being matured we understand that condition, in which by the effect of heat some of its constituents have been so far melted that they are able to cement the parts not melted without destroying the porous character and producing noticeable changes of form by too great softening. If the liquefaction be increased or long continued the influence of heat goes so far that a sufficient amount of a liquid vitreous mass is present to fill the pores of the clay, and at the same time to produce a noticeable softening. This is the condition in which we find the hard porcelain and clinkers; the process finally ends in the vanishing of all chemical differences and the formation of a glass or a slag.

This process of burning to a matured condition has for its purpose the formation of a certain small amount of liquid substance which physically and chemically we are wont to call glass. This strengthening, binding material, whose chemical nature is indifferent for our purpose and may be subject to the greatest variations, is formed in part by the melting of fusible compounds already present in the clay; in part it is the result of a chemical process which takes place during the burning, which must, however, never be very extensive if the earthy character of the clay is to be retained. The degree of heat necessary to

produce that degree of fusion in the clay to furnish the liquid binding material, becoming solid with the decreasing temperature, for those parts not affected by the heat is, in the first place, dependent on the chemical nature of the materials, but also on the distribution and the physical properties of the individual components, especially of the rock dust and sand, which, in general, are the only components quantitatively to be considered, in which there has been preserved during the process of weathering a part of the crystalline structure.

We lack accurate scientific investigation to show what influence the crystalline structure of silicic acid compounds have on their fusibility; however, from the great refractoriness that is possessed by some silicates found crystallized in nature, for instance feldspar and leucite, and in which such a high melting-point could not be expected from the experiences heretofore had, it seems clear that the molecular attraction present opposes liquefaction, which is always connected with a complete destruction of crystalline structure.

Even if this point cannot yet be definitely decided, there are positive observations that the crystalline condition noticeably weakens and retards purely chemical actions as we must assume them during the vitrification of clay, that some substances even show themselves indifferent in the highest degree to chemical influences when they appear in a crystalline condition.

Since in the hard burning of clay the most easily fusible constituent or that one which according to its composition and physical condition is disposed to a chemical change at the lowest temperature must furnish the cementing material and this may now be clay, now sand, now rock flour, the changes taking place cannot with certainty be determined until each one of these constituent parts in a certain material has been individually investigated with regard to the properties here coming into consideration, and such investigations, whose utility can not be overestimated in regard to the knowledge of the materials, would aid in clearing up what is so far one of the darkest chapters in the investigation of the properties of clays.

## III

The phenomena shown by the formation of crystals in the interior of burned clay ware, are essentially different from those that we can observe in the interior of moist clay deposits, and find an analogy in those that appear in freezing, because an exertion of force which develops in the interior of moist clay by the formation of crystals causes only a change in the form or condensation without destroying the continuity of the mass on account of the yielding of the material, whereas in the brittle condition of the dried, frozen and burned clay it always produces a loosening of the structure and breaking. The substances which, through the formation of crystals, cause disturbances in burned clay masses, cracking and exfoliation, are either soluble salts previously present in the clay that have escaped vitrification by too little burning, or they are a product of subsequent weathering, or they have gotten in accidentally, in the case of building brick, for instance, out of the lime or the water used in building the wall; they are chiefly sulphates, nitrates, carbonates, and chlorides of the alkalies, of lime and magnesium, however different these substances may be in their nature. The effect which they produce with the help of water in their migration within the burned clay, remains essentially the same, and although the phenomena under consideration are usually ascribed to the formation of saltpeter it must be stated that in the great majority of such cases there is no appearance of saltpeter or nitrates and that the same phenomenon may be produced by any soluble salt that has gotten into the pores of the clay from any cause whatever and that real nitrates are wont to appear only then when the clay at the same time furnishes the soil for the vegetation of low organisms, fungi, molds and infusoria.

Just as in the phenomena of the deposition of clay so also here the water brings about the change of place of the crystallizing substances and, here as there, if we follow the main channel of the water the places can easily be found where the greatest effect was concentrated. If we examine a burned piece of clay, for instance an ordinary brick, on the broken surface we

shall see in most cases that the component parts are not equally distributed but that some parts by their color, porosity and grain show themselves as such in which one of the constituents of the clay predominates. Going still further and examining the fracture of the brick with a magnifying glass, we may observe that in consequence of unequal shrinkage of the different separated constituents during drying and burning, spalling from the main body, breaks and fine cracks are shown around small stones and coarser sand grains, along the lines of separation between clayey and silty portions, in general in all those places in which there are homogeneous portions.

The liquid which causes the mobility of the salts crystallizing in the interior of the brick receives its motion chiefly from the fact that evaporation takes place to the greatest extent at the surface of the brick while it is either altogether excluded from the interior or, at any rate, is very limited. Through the capillary attraction of the porous mass the liquid is drawn outward from the interior, and in this way a circulation of the water is produced which will take the inverse direction on the entrance of water from without, together with the salts dissolved in it. The circulation of the water is, of course, most vigorous in those places in the brick where it finds the least resistance to its movement, that is, in the cracks and crevices, those places from which a further destruction is most easily possible and which at the same time furnish the most favorable place for the deposit of crystals, because here the space is most readily found for the formation of crystals as symmetrical as possible. If crystalline salts have once been separated at such a place the further process of crystallization will increase some crystals at the expense of the rest because smaller crystals are more easily dissolved than larger ones with a new accession of water, and because with the vanishing of a part of the solvent new formations are deposited with greater ease on the already present similarly crystallized substance than they could be by seeking new points of crystallization for themselves. The result of the pressure exerted upon the surrounding clay mass by such a collection of crystalline sub-

stance at places especially favored for making room for the formation of crystals will, from the brittleness of the same, never lead to a simple dislocation and change in structure as it would in the case of moist clay, but produces a break, cracking, exfoliation, all the more so, because, as a rule, only a slight resistance can be made to the pressure developing in the interior. It seems clear, therefore, that the disturbing effect of the crystal formation, saltpeter or whitewash, must be especially noticeable in such materials in which the soluble salts present have not been disturbed or volatilized by burning; such material has not reached that degree of firmness and resistance to weathering, that is necessary in a suitable building material. In a brick externally of good quality, destruction will not fail to occur if the formation of crystals is favored at some places by an easier circulation of the liquid, that is when the structure of the same does not show the greatest possible degree of homogeneity.

A homogeneous brick will also be unable to resist permanently the crystal-forming force, always seeking new points of attack for destruction, but it will be able to offer a much longer resistance than one not completely homogeneous, in which by drying and burning through disproportionate contraction a weakening of the cohesive force has taken place and at whose weakest places the destructive force can concentrate itself.

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### Incompleteness in the Investigation of Brick Clay

PROFESSOR CHAS. W. MESLOH, TRANSLATOR.

The later investigations by Bischof and Richters concerning the determination of the degree of refractoriness have so far thrown light upon this difficult subject, in which all scientific investigations seem to be in direct contradiction to practical experiences, as to prove that the melting-point of clays stands in a certain regular dependence upon their composition; and it cannot be denied that by this work an inestimable service

has been rendered, not only to the ceramic industry in general, but in a still higher degree to those branches of the industry that make use of fire clays for construction material ; that is, all those that need for their manipulation a very high degree of heat. The question now arises, how far these investigations may also be useful for other branches of the ceramic industry ; and we must confess that the conclusions from those investigations are not of such a nature that they can be applied to these branches without difficulty, and likely the range of the investigations has been overestimated. The position of the fire clays, as far as they are used in building furnaces, etc. (that is, as the lining of such places in which a very high heat is to be produced), is far different from those products which are subjected to the heating process but once—such as all products of fine and common pottery and brick making ; since in the former a change in chemical and physical relation, a change which is always connected with a decided, though undesired, change in shape, is to be avoided as much as possible ; while with the others, that is in the manufacture of products which are to resist the influence of atmospheric agencies, it is to be encouraged as much as possible. Hence, the demands which must be made on the properties of the material for these various uses will be very different and while in the production of *pottery* the chemical action of the various elements is to be encouraged for the production of as great a degree of homogeneity as possible and thereby obtain uniformity throughout ; for the production of *refactory material* a certain lack of homogeneity is desired, at least sufficient to retard a chemical action of the constituents on each other, which action finally effects a fusion.

In order not to give rise to misunderstanding it is necessary that I state this point somewhat more clearly.

As has been repeatedly stated, clay is not a homogeneous substance in a chemical sense, not a substance which may be considered the same even to the smallest particles, but a mixture of differently compounded substances of definite physical properties which can be considered homogeneous only in so far as the

corporeity of the bodies of the various substances lying side by side permits. Even if on superficial observation clay appears uniform under certain conditions we will still, by the aid of the microscope, be able to distinguish the clay mass from the lamellae of mica, sand grains, calcareous and silicious shells of lower organism, and it is thus shown to be non-homogeneous even if less prominently so; the condition of absolute homogeneity does not appear until the clay has been molten to a glass by the influence of heat.

This degree of homogeneity brought about by complete liquefaction is never aimed at in the case of refractory material, and in the use of clay for pottery ware only to a certain degree; namely, so far as the shape of the objects to be produced can suffer no, or at least no essential, change through the condition of softening that precedes complete melting. No liquefaction is therefore wanted that affects the whole mass of the clay substance, but only in part, and the manipulation of the clay and the making it homogeneous has for its object the distribution of the part to be liquefied uniformly through the whole mass.

In the manufacture of refractory materials a certain lack of homogeneity is intentionally produced by giving the mass as few points of contact as possible from which melting proceeds and by producing a physical condition that opposes a certain resistance to liquefaction.

Clays which are used for the production of such objects which are to bid defiance to the highest degree of heat, are chemically and physically very different from those to be employed for pottery ware. In the case of the former we have to do with a mass that consists relatively of a pure and uniform substance, which has as the chief constituent only one definite combination of aluminum oxide and silicic acid, and flux, which, according to the relation in which these parts stand to each other, offer greater or less chances for great refractory power, while the non-plastic materials accompanying the real clay substance, are either quantitatively inconsiderable or show the refractoriness of the fundamental mass.

For the production of pottery ware, bricks, etc.,—in fact, all such products which are burned only to give them resistance to the influence of air and moisture, a certain difference in the fusibility of the component parts is always required so that the one part is not affected by the heat to which the object is exposed, and forms, as it were, the firm skeleton which preserves the form of the objects, while the other melts and in this shape is entirely indifferent to atmospheric influences after cooling, surrounding and protecting the unmelted portions.

While, therefore, in the case of the refractory materials which are to resist a high degree of heat for a long time, we shall demand a certain uniformity in the degree of its refractoriness; we demand, on the contrary, for the other uses of clay that certain constituents of the mass possess a comparatively low melting-point, while the other constituents are less sensitive to the influence of heat.

If, in respect to physical and chemical qualities, we compare the materials which serve for the manufacture of building material with those which are destined to offer the greatest resistance to fire on the one hand, and on the other hand to water, that is on the one hand the plastic refractory clays, on the other hand the brick clays, they may be essentially described as follows:

With regard to the principal mass, plastic clays consist of the weathering products of a certain kind of mineral or rock, which according to its origin has a varying quantitative composition, but always consists in the main of that peculiar combination—alumina and silicic acid—which we call clay substance, while other contaminating substances are less important and have no essential influence on the properties. It is different, however, with the brick clays. These, likewise, contain clay substance in a greater or less degree which gives to them the characteristic property of plasticity. It is, however, mixed in such a manner with the débris of rocks in the form of rock dust and sand whose origin is for the most part not even found in the same mineral as that of the clay substance, that these non-plastic substances, even if they do not always predominate

quantitatively, are still so strongly represented that their properties, differing from those of the clay substance, have always an essential influence on the properties of the whole.

If the chemical analysis has discovered a fixed relation between alumina, silicic acid, and flux, we know that these constituents belong essentially to a single well characterized combination so that we can take the degree of refractoriness from the laws established by Bischof and Richters with a greater or less assurance, according as this substance is present in a greater or less degree of purity. However, if we should proceed in a similar way in the investigation of brick clays we would get a theoretical result so very different from the practical result that it would have no value whatever in regard to the knowledge of the material. The chemical analysis gives us only an average of the composition of the components forming the clay, differing very widely in their chemical composition and their physical properties. Since the clay, after burning, preserves its earthy character and the various constituents act only superficially on each other, the chemical analysis gives us absolutely no clue for the deduction of definite properties of the whole.

Two brick clays may have exactly the same composition and still differ in every respect, because the complete analysis, for example, gives us no idea whatever as to how much silicic acid, alumina, and flux belong to the clay substance, to the rock dust, and the sand individually; for instance, in the one case all or the greatest part of the flux may belong to the clay substance, in another case to the constituents which make clays lean, and accordingly the properties of the compound be subject to the greatest variation with the same percentage composition. In the one case it may be the clay, in another the rock dust or sand, which, with the same percentage composition of the whole, is the most fusible constituent; or it may be some accessory constituents, as admixed iron oxide or carbonate of lime, which according to the manner of distribution are inclined to have the strongest effect sometimes on the clay, sometimes on the rock dust and sand, and thereby produce

a number of variations which find not the slightest explanation by a simple chemical analysis.

If we conclude from this that the chemical analysis can claim only a limited value for the discovery of the properties of brick clay, such a judgment would be highly one-sided and inaccurate. For such uses of clay in which it loses completely its earthy character, as in the manufacture of Portland cement or glass, the chemical constitution is first considered, and the other physical properties only in so far as they are able to give a greater or less resistance to the destruction of its earthy character; and here the chemical analysis alone is able to give information concerning the utility in this direction. For our purposes it is especially the physical properties of clay that are of greatest importance in judging the same, and the chemical properties only as far as they supplement the former. Here, therefore, to express it in a few words, it will be the task of the chemical analyst to determine the composition of the constituents that are physically alike, that is of the clay, rock dust, sand, accessory constituents, separately and singly, and to make possible a comparison of these with each other. In this way we are able to get a good idea of the properties of the components, whereas an analysis of the whole mass would be of little use. We are thus convinced of the necessity of physical analysis of clay simultaneously with or rather before the chemical, as far as the investigation is made for the purposes of pottery ware, and especially for the manufacture of bricks. Even though scientific men have repeatedly referred to the importance of the mechanical and physical investigations this direction of the investigation has not been pursued with such vigor that the results obtained from it show any real use for the brick industry.

If we examine more carefully the analyses of clays, both plastic and brick, as we find them in many chemical and technical works, we find that they are either only a summary enumeration of constituents, silicic acid, alumina, lime, oxide of iron, etc., in per cent., or even in the most favorable case, beside the

analysis of the washed mass, that is of the clay substance in the purest state obtainable, a statement that certain percentages of dust and sand were also contained in it.

For the investigation of very pure clays, where the percentage content of non-plastic substances naturally contained in them is only very small, this may suffice as being of no great importance, but when the proportion of sand is given as 60 or more per cent, without stating of what the sand consists, what influence it may have on the properties of clay, and what its physical and mineralogical properties are (and this I have not found in a single one of many analyses) this is certainly a defect which brings the value of such investigations to naught and makes them appear only in the light of analytical exercises.

Such investigations will have a real practical value for the industries, only when we accustom ourselves to look upon clay as it really is,—even in the condition of the greatest homogeneity that can be obtained by mechanical means,—namely, as an aggregation of different grains lying side by side, independent of a definite chemical composition, whose physical properties give certain characteristics to the whole, that make it possible to make a definite use of them, in which a change by the influence of burning is not to extend uniformly to all parts, but only to some especially disposed to such a change, while the other parts are to be affected only at the points of contact. If one should carry the effect of burning still farther we should no longer obtain the desired product but, instead of an object in which the vitrification is only to appear as begun and whose earthy character is to be preserved, we would get a perfect glass devoid of its earthy character.

I believe I have sufficiently indicated above what is to be aimed at in the investigation of impure clays (that is, brick clays) if it is to justify us in making such conclusions, at least approximately, which Bischof and Richters could draw from their results concerning refractory clays in reference to these comparatively very rare clays. It would be necessary to only carry out a strict separation as far as possible of the unlike constituents

having a different value and treat these as of equal importance. In fact, I cannot understand why, in the analyses which we have, if a separation took place at all it was always the plastic substance to which the whole attention of the investigation was directed, while the non-plastic parts were treated as though the knowledge of their properties were a matter of course. But are we not compelled to measure these as given and necessary factors by the same rule as the former? or do the non-plastic parts of clay not allow the same variety to be presupposed as the plastic parts?

The preparation for such far-reaching investigations of clay which from a series of results that could be compared with each other would allow just as definite laws to be deduced for the properties of brick clays, as Bischof and Richters have furnished them for plastic clays, even if the investigation would be still more complicated, is furnished by the mechanical analysis of clay by means of the washing process; and if this has been given only a very subordinate rank in the investigation of the properties of clays, the reason may, for the most part, be found in this, that the methods of the investigation used for this purpose have been so deficient and have furnished results so far from agreement that its value was very properly looked upon as very small.

However deficient may be a separation of the unlike components into parts that are approximately alike physically, still a more general use of this method would have given more clearness to the views concerning the behavior of clay, while the numerous analyses have not advanced us a single step, and if we have lately received such an apparatus, in the Schoene washing apparatus, which permits a much sharper and more convenient separation than was formerly possible, it is an acquisition which cannot be overestimated.

It is not only the chemical investigation of the individual components of clay that is of weight in judging it, but perhaps in a still higher degree the mechanical investigation. The knowledge of the structure of the clay, the average size of the grains of sand, their form as to whether they are round,

ground or splintered, or lamellae, the degree of cohesion, the plasticity of clay, the amount of shrinkage on drying and burning, its porosity and water-holding power, its hydroscopic properties, the occurrence and the kind of interdeposition of chance admixtures—all these are questions concerning which chemical analyses can give us no information whatever, and yet they are of the same, for the most part perhaps, of greater importance than the knowledge of the chemical composition. These questions may be answered only by careful observation made at the place of deposition itself by the most subtle observation with microscope and magnifying glass, scales and washing apparatus and offer such a variety that much study is necessary to be able to answer them in a satisfactory manner.

I am convinced that these questions are highly urgent for the interests of brick-makers in order to explain the variety of the phenomena which appear in the preparation and manipulation of clays; but all the scientific investigations give us no help in this regard. We know nothing concerning the mutual relations between the degree of moisture of the clay and its contraction and cracking; nothing of the relation existing between the size of the grain and the amount of the non-plastic substances and the porosity and water-holding power, and it will take many a year of the most troublesome investigation and diligent study before results satisfactory to practice appear in this direction, so completely neglected up to this time.

I am not reproaching science for not having cultivated this field at all, at least not for the purpose of the clay industries, and will not ascribe to science the responsibility for these gaps whose presence we cannot deny; as we see in many branches of technology that make use of science, scientific investigations prosper only where they were not undertaken on their own account, but where the industries approached it with definite questions and with a well defined aim. If the clay industries have up to this time not come with questions of this sort and only now are timidly approaching, the cause is to be found in the fact that they themselves were not able to indicate the aims for which they are striving.

In pointing out the great gaps which scientific treatment shows in regard to the knowledge of clay, it is not my intention to describe a definite way for such investigations, but rather to cause the practical man to formulate accurately his questions and his needs and to point out the fact that a few investigations carried out in the manner indicated above can be of far greater utility and give much greater interest to the questions stirring the industries than the many half and one-sided ones that we already possess.

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### The Mechanical Analysis of Clay

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PROF. CHAS. W. MESLOH, TRANSLATOR

I have indicated in the previous chapter how deficient the information is, which chemical analysis alone gives for the knowledge of the properties of clay, if this is not supported by a mechanical separation of the different parts by mechanical analysis. Through the excellent work of Mr. W. Schuetze we have learned how to obtain such a separation, how to easily carry out a separation of the constituents of clays within certain limits with scientific exactness. The lack of regard for the physical properties has been one of the chief reasons why science has not been able to explain many peculiarities of clay bodies, and that the conclusions derived from a chemical analysis were often in direct contradiction to practical experience; and if these gaps cannot be at once filled out, the cause for it lies in the fact that only comparatively few, and for the most part incomplete, investigations are at hand. This lies in the nature of the chemical investigation; since it has been inaccessible to mathematical treatment which bases itself on few observations, it requires a great number of direct observations to be able to deduce laws from them.

Hence, if I communicate a few mechanical analyses, it is not done with the intention of deducing from them far-reach-

ing conclusions which can be obtained only from a large number of observations, but rather to determine certain definite conceptions for such constituents of clay whose physical properties differ very essentially from each other.

We are accustomed to consider as clay substance those parts which show the greatest decomposition, in which the extraordinary extent of surface brings about that peculiar phenomenon of surface attraction that we call plasticity, which shows in its exterior, in a much higher degree, all the peculiarities which we observe in clay in the ordinary sense of the word.

This peculiar clay substance, even if it does not make up the whole mass, is contained in those products which can most easily be washed out of the clay and remain suspended longest in the water. Since all apparatus show certain imperfections and in nature there are no leaps from the finest to the coarse, but all intermediate stages are to be found, it is necessary to come to some agreement as to where the unavoidable divisions are to be made. In the determinations communicated below, that portion was called clay substance which was carried away by means of the best washing apparatus, namely Schoene's, with the smallest velocity of the current that could be determined to a certainty : This is 0.18 mm. per second with 20 mm. pressure in the piezometer according to the magnitude calculated by Schoene for the velocity of quartz balls falling in water and from the direct microscopic measurements of the products of washing from his apparatus, this velocity would indicate a maximum size of the grain of 0.010 mm.

The part not separated from the clay with this smallest velocity shows qualities essentially different from the real clay substance. I have designated it as rock dust. This consists of small mineral fragments so fine that on rubbing between the wet fingers they still cause a slippery feeling. With water it forms a somewhat plastic but short mass which on drying shows but little coherence and remains dull on rubbing with the finger nail, while the clay substance, with a similar treatment, assumes a fine polish. Under the designation of rock dust come all ma-

terials that have a size of grain between 0.010 and 0.025 mm. in diameter and can be washed out with a velocity of 0.70 mm. per second.

The next coarser particles are designated as silt, since through the touch of feeling a sandy character is hardly recognizable while physically it shows itself as such. To this dust-like sand corresponds a velocity of 1.5 mm. per second, 900 mm. pressure in the piezometer and a grain of 0.025 - 0.040 mm.

As fine sand are designated the particles whose grain has a diameter up to 0.333 mm.; as coarse sand everything above this.

The clays investigated differ widely in their qualities. The one marked "A" is an extremely unctuous and refractory clay of the lignite formations of Senftenberg in eastern Prussia of a grayish white color. Clay "B" is from the same place found in alternate layers with the former and is characterized just as much by great fineness as by its shortness. "C" is a refractory clay from Grenzhausen in Nassau, as it is used without any further addition or manipulation for the production of the wares of this district that are valued so highly for their durability. "D," finally, is a ferruginous clay alternating with strata of loam at the northern edge of Berlin, unctuous and full of sharp grains of sand, contracting very much on drying and badly cracking.

The given characteristics find their expression again in their analyses by washing.

The four clays "A" from Senftenberg (unctuous), "B" from Senftenberg (short), "C" from Grenzhausen, and "D" from Berlin, gave:

	A Per cent.	B Per cent.	C Per cent.	D Per cent.
Coarse sand with grains over 0.333 mm.	0.58	0.34	0.18	21.20
Fine sand from 0.333 to 0.040 mm.	3.00	28.46	10.64	11.58
Silt from 0.040 to 0.025 mm.	3.52	13.84	9.08	1.84
Rock dust from 0.025 to 0.010 mm.	11.16	20.24	10.88	2.14
Clay substance from 0.010 to 0.000 mm.	82.18	37.10	68.32	62.00
	100.44	99.98	99.10	98.76

A comparison of the given figures permits us to draw some conclusions in regard to the quality of the material. While in the most plastic of the clays investigated, the Senftenberg clay marked "A", the greatest content of clay substance appears and besides this only the finest mineral fragments are found, with the others the fine and finest non-plastic constituents are more prominent and give rise to their character as short and less plastic materials without depriving them of all the good qualities of plasticity and fineness. With the Berlin clay, however, besides the plastic mass the relatively coarse non-plastic parts appear more prominently while the finer ones nearly vanish completely; with these, properties at once appear that do not exactly recommend it.

It cannot be doubted that the valuation of the material is made so difficult only by the variety of the constituents which causes these differences, by the size of the grain, the shape, character of the surface, and the mutual relation of the same. As long as comprehensive and systematic investigations have not been made in this direction which permit safe conclusions from a large number of observations, the phenomena of shrinking, cracking, porosity, of water-holding power, and absorption of water must remain unexplained and practice must grope in the dark as heretofore. Unfortunately the number of accessible observations is so very small that for the present they can be of little practical utility until they get their full value through further observations.

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#### Note on the Use of Schoene's Washing Apparatus

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PROF. CHAS. W. MESLOH, TRANSLATOR

However good results Schoene's washing apparatus furnishes in separating substances of different sized grains, the use of it is apt to result in error, especially when the problem requires the separation of the finest washed substances from the

sandy and silty part, but less so with the separation of the coarser grained material which requires the application of a greater velocity.

If for the purpose of a mechanical analysis we put the clay to be washed, completely broken up by continued boiling and freed from all root fibers and coarse sand, through a sieve having meshes of 0.2 mm., into Schoene's washing funnel and begin the washing operation with the precautionary measures described by Schuetze in the *Notizblatt*, 1871, 7, 307, and 1872, 8, 185, to remove the finest clay substance, there is formed in the lower part of the washing funnel a deposit of sand and finer parts because the slight velocity is not able to keep these parts suspended. The lower end of the washing funnel shows how this deposition takes place; with the precipitated sand not only rock flour, but frequently also the finest clay substance, is frequently thrown down, and so escapes washing and removal.

If for the purpose of removing the rock flour and dust-like sand the current is increased, the more powerful current of water often passes over this sandy deposit without completely causing its suspension, and it often needs a continued tapping with the finger or a strong supply of the washing water in a jet, after stopping the supply of water for a time, to drive away the deposited sand and cause it to be suspended in the lower part of the washing funnel in the quickly rising current of the water.

Naturally, reliable results can only be obtained when all parts are incessantly exposed to the current of water and an incomplete separation sometimes appears as a result of the evil mentioned, since the liquid, by means of which the rock dust-like sand and fine sand were carried over, does not appear clear after standing awhile, but often has a milky color for days, whereas with a thorough manipulation of the washing analysis a complete clearing has often taken place after a quarter of an hour by the precipitation of the sandy parts. By means of a little artifice the evil mentioned may be avoided with ease and certainty, and anybody who works with a washing apparatus is able to make the little auxiliary apparatus himself.

Into the lower part of the washing funnel "A" a piece of cork is introduced into which a hole from 5 to 8 mm. has been bored and filed out upward in the shape of a funnel with edges as sharp as possible. The lower round opening is closed by means of a little brass sieve  $\alpha$ , having meshes of 0.2 mm. which is cemented under the cork by means of sealing-wax. In consequence of the small size of the many openings through which the water streams into the washing funnel, its velocity is so great that no sand particles can get through the sieve into the lowest curved part and be deposited there, but they remain in constant violent agitation in the interior of the funnel-shaped cork or suspended freely in the water above it during the whole process, even with the smallest velocity.

If one is careful to cause an extremely weak current of water in the washing funnel before pouring in the clay, nothing will get under the sieve and a very sharp separation of the parts carried above it by the current of water is made possible. Even when the water is cut off completely nothing or at any rate only a few coarse grains which cannot be lifted out of the apparatus by the current of water will fall through the sieve.

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### Notes on the Chemical Constitution of Clays

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PROF. CHAS. W. MESLOH, TRANSLATOR

However valuable the data are, which the physical investigation of clays offers in regard to their behavior in the plastic condition, in drying and soft burning, however valuable the chemical analysis is for the recognition of the constituents which prove harmful in the manufacture, as in the investigations of Bischof and Richters for the judging of the degree of fusibility, these investigations do not yet suffice in all cases for characterizing sharply the character of a clay or a body for clay wares, and it happens often enough that the scientific results and the discoveries of practice deviate more or less from one another. It is therefore necessary in many cases to confirm or to supplement

the results obtained by science, by practical tests which are similar to those used in the industries. The cause for this is found in the fact that the chemical and physical analyses allow only a few mutual relations to be seen and do not give information concerning all conditions. The physical analysis teaches us to know the relations between the clay substance and the unweathered mineral fragments of varying size, and explains a series of phenomena that are more or less independent of the chemical composition. The chemical analysis gives us hardly any information concerning physical properties, and for the behavior in high temperatures conclusions are only possible under the presupposition, that all substances indicated by the chemical analysis can enter into action. This, however, is not often the case, especially when the clay contains coarse ingredients of any kind whatever, and in these cases the result of the chemical analysis will always have to be corrected by further experiments adopted to the practical use. Both methods of investigation, therefore, do not permit us to recognize sufficiently well the character of the clay.

This apparent contradiction between the results of scientific investigation and the phenomena found in practice is very plainly illustrated by the experiments that were made in Sèvres which aimed to produce hard Chinese porcelain according to the results of chemical analysis. Brogniart reports that in these experiments the constituents of porcelain, that is, silicic acid, alumina, alkalies, etc., mixed in the proper proportions, gave no porcelain in the porcelain fire, but only a white enamel. From this we see that not only the individual constituents of a clay mass have an influence on the properties according to their quality and quantity, but that the compounds ready formed in it have an influence through their chemical as well as through their physical differences on the properties of the whole.

In general we can look upon clay as a mixture of quartz grains, unweathered mineral fragments, and the weathering product of the latter, the clay substance (for the most part silicate of alumina containing water). Since the two latter substances

may be very different, not only qualitatively but also quantitatively, and in reference to their size of grain show great fluctuations, it is clear that we can only then speak of an accurate knowledge of clay when we succeed in determining these constituents according to their kind and amount in the clay or in bodies.

In the case of the bodies employed for the finer branches of the clay industries, the internal constitution is better known to us, because the raw materials used here are always as pure as possible and, in part, also chemically well definable.

Bodies for hard porcelain are for the most part composed of three constituents: quartz, feldspar, kaolin. Quartz consists essentially of crystalline silicic acid, feldspar of a combination of silicic acid, alumina, and alkalies (potassium, sodium sometimes partially replaced by calcium and magnesium oxide); kaolin consists of the same constituents in a different proportion with generally only small amounts of alkalies besides water. The latter is not considered in the chemical composition of porcelain. If we now know the chemical composition of a porcelain body, that is of quartz, feldspar, and kaolin, and wish to compose from it a porcelain of definite elementary composition we could cause these three constituents to vary in several proportions, since they all contain the one or the other substance in common, without causing great differences to appear in the chemical composition of the whole. Nevertheless, the properties of the mass, according as one or the other of the essential constituents becomes more prominent quantitatively, would differ very much in spite of the same chemical composition of the whole. In practice, the materials used are never in such a condition that they can be looked upon as pure chemical combinations. With quartz or powdered flint, and so on, and with feldspar, this may be the case; rarely however with kaolin, which even, when washed very fine, contains more or less large parts of the rock formation from which it has originated, especially fragments of quartz and feldspar that have escaped weathering. Since the bodies are formed empirically, the natural content of

quartz and feldspar in kaolin however is unknown according to the method of investigation heretofore employed, and cannot be taken directly from the analysis; the conditions are changed with the change of the source and new proportions, and often new experiments are made necessary. This would, however, not be necessary if one could determine in advance the relations between quartz, feldspar, and the real clay substance in kaolin. For those branches of the clay industries that compound their bodies from raw materials which have definite sources and constant properties, it is not difficult to cause the properties of the body to vary empirically within certain limits by a change in the proportion. Much more difficult is it for those industries that work up raw material of less pronounced individuality as plastic clay, potter's clay, brick clay, which on the occasion of a natural washing process have taken up foreign substances not belonging to the original product of weathering and in which therefore clays lying near to or above one another show great differences. The former, to be sure, need a greater amount of artificial manipulation, yet it cannot be denied that with reference to the production of the body the latter produce greater difficulties in manufacture, and I have heard it stated by a competent professional, that it is much easier to produce a faultless white porcelain or stoneware than terra cotta or tile of a definite color and strength, in case one is compelled to use raw materials wholly unknown as to their peculiarities.

These difficulties, which the lack of knowledge of the properties of the materials to be used cause in the one direction or the other, are for the most part to be overcome only by empirical experiments which cost much time and money and cause disturbances in the regular running of the factory. They would be essentially diminished by a better knowledge of the inner constitution of clays, through the knowledge of the distribution of constituents, as indicated by chemical analysis in the constantly recurring essential constituents, differing from one another in their chemical and physical properties; by knowing which belong to the constituent that does not weather at all,

yielding to all chemical influences only at the highest temperatures, as quartz; which belong to constituents capable of weathering, as the mineral fragments (feldspar, etc.); and which to the real clay substance in the widest sense, the product of decomposition of all argillaceous minerals.

Such a further knowledge of the essential constituents of clay has been aimed at by several investigators and finds its expression in the so-called 'rational' analysis of clays. This is based on the different chemical behavior of mineralogically different constituents of clay, but has for the most part found application only in the determination of the chemical constitution of the real clay substance, while the other constituents, excepting the free amorphous silicic acid, have not found that consideration which they deserve. Due regard for this seems all the more desirable in the clay industries, since the constituents which from their physical properties are not to be looked upon as clay, are present even in the purest clay, the washed kaolin, and in a considerable proportion in the unctuous plastic clays, while with the more impure clays and the brick clays they amount, for the most part, to more than half of the whole mass.

According to the example of Forchhammer and Fresenius, a series of porcelain earths and plastic clays have been investigated in the direction indicated and published, in order to make clear the process taking place in the weathering of feldspar into clay. The method of investigation is based on the fact that the product of the weathering of feldspar (that is, the real clay) is completely decomposed under the influence of sulphuric acid at a high temperature, while quartz, feldspar, and other minerals rich in silicic acid, occurring in it, are unaffected, so that it is at least possible to separate the one constituent, the clay substance, and examine it more closely with regard to its constitution.

We find furthermore in the literature a number of clay analyses in which the real clay substance is indicated in its composition together with free silicic acid and the parts soluble in hydrochloric acid, and in which the undecomposed mineral frag-

ments have been entered under the heading "insoluble residue," without examining their composition more carefully. Other analytical chemists have made use of the same method to determine the various conditions in which silicic acid is found in all clays and in which it also possesses different properties, as chemically combined silicic acid, amorphous silicic acid set free by weathering, or as crystalline silicic acid (quartz sand). Among these analytical chemists are found also Bischof and Richter to whom we owe a large number of carefully executed analyses of clay. In these analyses, that part of the clays insoluble in sulphuric acid is simply looked upon as quartz sand and calculated as free crystalline silicic acid. For the determination of the silicic acid present as quartz the method is, however, admissible only if the clay, besides clay substance, contains only quartz and no other minerals not decomposed by sulphuric acid. As the analyses below will show, the residues which remain after the breaking up of the clay substance by sulphuric acid and which have been entered as quartz in the analyses by some chemists, do not, in most cases consist of pure silicic acid, but contain also amounts of alumina and alkalies, which can not be neglected, and which give to them the character of mixtures of quartz with silicates of alumina.

In a former consideration of the various methods of investigation of clay and the conclusions to be drawn from them, Aron has pointed out the great importance for practical purposes of the rational analysis, used heretofore only for purely scientific purposes in connection with the chemical analysis of elements and the physical analysis, which remains justified; this has induced the author to examine this method of investigation more carefully, and not only in the direction of determining the amount and composition of clay substance, but also the mutual relation of quartz to undecomposed feldspar and other minerals in order to get some clearness in this direction also.

Now, before the investigation of a series of clays could be undertaken in this way, the method itself had to be subjected to a trial as to whether and under what circumstances a complete

decomposition and separation of the clay substance from the undecomposed mineral fragments is possible, and in how far the latter, especially feldspar, are able to offer resistance to the action of the reagent employed. For this purpose clays of very different chemical and physical constitution were exposed to the action of sulphuric acid for different lengths of time, and it was noted after what interval of time the residue produced by the decomposition remained constant; that is, when the action was complete. There were selected for this experiment the extremely unctuous pot clay of Gruenstadt and the very short brick clay of Schwarzehuette near Osterode in the Hartz mountains.

Of each of these clays three samples of about 2 grams were weighed, boiled with water in a platinum dish until fully broken up, then mixed with 10 cc. of concentrated sulphuric acid and heated, first on a water-bath, then on the open flame until the excess of sulphuric acid was completely evaporated at such a rate that the action of the sulphuric acid lasted from five to six hours near its boiling-point, that is at about 300° C. With the one sample nothing more was done; with the second the dry residue was mixed with concentrated sulphuric acid to a thin paste and again exposed from five or six hours to the action of sulphuric acid at about 300° C.; with the third sample this operation was repeated once more so that the time of the action of hot sulphuric acid amounted respectively to from five to six, ten to twelve, and fifteen to eighteen hours. Thereupon the samples were boiled first with water, then twice alternately with a solution of caustic soda and dilute hydrochloric acid for the removal of the sulphates formed and the silicic acid that had been separated out; the remaining sandy residue was collected on a filter, washed, ignited, and weighed.

The following table gives the amounts of the residues remaining:

Time of the action of sulphuric acid.	5 to 6 hours.	10-12 hours.	15-18 hours.
	Per cent.	Per cent.	Per cent.
On the Gruenstadt clay.....	8.64	7.79	7.69
On the brick clay from Schwarzehuette	76.41	66.71	66.86

We see from this that after the second evaporation of the sulphuric acid, that is after an action of from ten to twelve hours, the decomposition may be regarded as completed, and that, however, an action of five to six hours does not seem sufficient. In order to be altogether certain the action was extended to from fifteen to eighteen hours in the experiments following; the product of the first action of the sulphuric acid was twice mixed with the concentrated sulphuric acid to a thin paste and the sulphuric acid evaporated.

In order to determine whether the residues remaining really consisted only of the quartz or whether they contained other minerals, they were stirred with some dilute sulphuric and hydrofluoric acids for some time, then by heating the excess, hydrofluoric acid, silicon fluoride and sulphuric acid were driven off and the residue of aluminum sulphate and alkaline sulphates was weighed. It amounted in the case of the Gruenstadt clay to 0.26 per cent, and in the brick clay from Schwarzehuette, 8.54 per cent.

We see from this that while the residue in the case of the one clay actually consists almost entirely of quartz, as was assumed in most analyses in which the same process was employed, the residue in the case of the second contains appreciable amounts of basic material and other minerals not decomposed by sulphuric acid, which, however, would most likely show a different behavior in the fire than quartz.

In the same way a powdered sample from a firm and apparently unweathered feldspar crystal was treated. It showed a residue of 97.76 per cent. This slight attack of sulphuric acid need not be regarded practically, and it remains doubtful, at any rate, whether it is not to be referred to a slight weathering, so that under the given circumstances we may regard feldspar as being not attacked by sulphuric acid.

In the case of those clays that owe their origin to the weathering of feldspathic rocks and have not yet experienced a natural washing, it may be expected that they still contain a greater or less proportion of unweathered feldspar besides the clay sub-

stance and the quartz; in the case of clays found in secondary beds, other substances are usually added. It would therefore be important, not only for scientific, but in a higher degree for practical purposes, to possess a method of determining directly, at least approximately, the amount of undecomposed minerals besides quartz and to determine their nature. Unfortunately such a method is not yet in existence, and the author has not succeeded in determining quartz and feldspar side by side in a manner even only approximately, except indirectly by the determination of the silicic acid and the alumina.

A direct separation of quartz and silicates was attempted by the melting of quartz and pure feldspar powder with boric acid, vitreous phosphoric acid and phosphorus salts, and it was shown that on the one hand the quartz is dissolved by these substances to a considerable degree in igneous fusion; on the other hand that the decomposition of feldspar was only very incomplete even after a long action. Therefore the direct chemical separation of the quartz from other mineral fragments was given up, and the composition of the residue insoluble in sulphuric acid was determined by decomposing it with four times its weight of potassium and sodium carbonate which succeeds very well with the invariably high content of silicic acid without previous powdering and, therefore, without loss of substance. This mass was dissolved in water, the silicic acid completely separated with hydrochloric acid and subsequent evaporation; after filtering off the silicic acid the alumina, which in the case of the impure brick clays sometimes contains iron, was separated out by twice precipitating it with ammonia and the remainder calculated as alkali.

If one is certain of having only quartz and feldspar to deal with, a determination of both may be carried out with scientific accuracy by calculation,—but not when other minerals are present. For practical purposes one will get determinations sufficiently accurate when for such mineral fragments one calculates as much silicic acid for the proportion of alumina as corresponds to the composition of feldspar.

In all further investigations the amount of mineral fragments is calculated out of the amount of alumina as if it were derived only from feldspar.\*

### I

The following analyses of kaolins carried out in this way and compared with an analysis of the porcelain body of the Royal Porcelain factory in Charlottenburg, will make clear the practical importance of the method of investigation.

There were investigated:

1. Kaolin from Ledez near Pilsen, washed.
2. Kaolin from Kottiken near Pilsen, washed.
3. Body from the Royal Porcelain factory in Charlottenburg.

Results.	1		2		3	
	Total amount.	Insoluble in H <sub>2</sub> SO <sub>4</sub>	Total amount.	Insoluble in H <sub>2</sub> SO <sub>4</sub>	Total amount.	Insoluble in H <sub>2</sub> SO <sub>4</sub>
Silicic acid -	49.16	9.05	49.91	10.65	63.07	38.09
Alumina -	36.73	1.70	35.99	1.21	24.67	4.15
Ferric oxide -	0.81		0.63		0.59	
Calcium oxide -	trace		0.00		0.00	
Magnesium oxide	0.18		0.30		0.40	
Potash -	1.18	0.99	0.76	0.73	4.25	2.84
Water -	12.41		12.34		7.00	
	100.50	11.74	99.93	12.59	99.98	45.08 .

These figures at first admit of no comparison and nothing indicates that we have to do here with mixtures of the same materials, quartz, feldspar, and clay substance only in different proportions of mixture. If, however, from the composition of the part not soluble in sulphuric acid, we calculate, on the one hand the relation between quartz and feldspar (1 per cent of

\* Note.—According to a later proposition by Dr. Lindhorst ("Thon-Industrie Zeitung," (1878) 2, 435) the residue insoluble in sulphuric acid is broken up with hydrofluoric acid and thereby a quantitative determination of the potassium and sodium content of the unweathered rock is made possible. This method has since been adopted by Seger and is now the only one used.—*The publishers.*

alumina corresponds to 3.51 per cent of silicic acid derived from feldspar), and on the other hand the composition of the real clay substance, then the analyses gain very much in clearness.

	1. Kaolin from Ledez. Per cent.	2. Kaolin from Kottiken. Per cent.	3. Porcelain body from Charlottenberg. Per cent.			
Quartz - - -	5.08	6.40	23.52			
Feldspathic resid'e	8.65	6.19	21.56			
Clay substance - - -	86.27	87.41	54.92			
	100.00	100.00	100.00			
The clay substance contains:		Oxygen content.		Oxygen content.	Oxygen content.	
Silicic acid - - -	40.11	21.39	40.26	21.41	24.98	13.32
Alumina - - -	35.03	16.39	34.78	16.27	20.52	9.60
Ferric oxide - - -	0.81	0.24	0.63	0.19	0.59	0.18
Calcium oxide - - -	0.00	0.00	0.00	0.00	0.00	0.00
Magnesium oxide - - -	0.18	0.07	0.30	0.12	0.40	0.16
Alkalies - - -	0.19	0.03	0.03	0.00	1.41	0.24
Water - - -	12.41	11.03	12.42	11.03	7.00	6.22

If from the amounts of oxygen contained in the second columns we calculate the chemical formulae of the clay substances assuming that the sesquioxides (oxides of aluminum and iron) and the monoxides (magnesia, potassium, and water) mutually displace each other, we obtain the following equivalent proportions:

	Silicic acid.	Alumina.	Water.
1. Kaolin - - -	1.92	: I :	2.01
2. Kaolin - - -	1.95	: I :	2.08
3. Porcelain body - - -	2.04	: I :	2.04

The clay substance of all three materials investigated is, therefore, to be considered as identical in its chemical composition and corresponds to the formulas of clay substance set up by Forchhammer for the product of decomposition of feldspar:



There is, however, a difference between the clay substances in so far as with them an unequal amount of water is displaced by fixed alkalies which according to their amounts must exer-

cise a varying influence as fluxes at high temperatures. If we omit water and calculate the proportion between fluxes, alumina and silicic acid, as Bischof does for the determination of the quotient of refractoriness, we obtain the following numbers:

To one equivalent of flux there are contained in

1. Kaolin of Ledez	-	55.43 equiv. $\text{Al}_2\text{O}_3$ , and 106.95 equiv. $\text{SiO}_2$ .
2. Kaolin of Kottiken	-	45.71 " " " 89.25 " "
3. Body from Charlottenburg	7.76	" " " 15.85 " "

Such simple relations and such a clear idea of the inner constitution as a rational analysis can furnish, in connection with elementary analysis, in the case of kaolins, we can, of course, not expect in the case of clays of a secondary or tertiary bed; on the one hand, because in the most cases the original rock forming the clay can not be found, and hence we can not determine the simple relations as they exist between the feldspar and the clay substance of the primary kaolin; on the other hand, because, through percolation, substances have for the most part been added, that exert a considerable influence on the property of the clay, but from their nature can not be distinguished separately from the mixture. In the two following tables are, first, four clays, which, coming from the lignite formations, are to be classed with the purer clays, and belonging to the lower stages of the refractory scale are used for the manufacture of light-colored face brick and stoneware products; and second, four brick clays, free from lime, which have proved especially fitted for the manufacture of paving brick.

The process of investigation is similar to that described for kaolin. In place of feldspar being associated with quartz and clay substance, other silicates will appear, especially in the brick clays. Since these, however, from their nature, can be only compounds containing much silicic acid, we shall not be much in error if we assume the same silicic acid content for them as exists in feldspar; that is, for 1 per cent of the alumina and iron oxide present in the residues, not decomposed by sulphuric acid, 3.51 per cent of silicic acid is assumed to belong to the undecomposed mineral fragments and the rest of the silicic acid is given as quartz.

## II

## LIGNITE CLAYS FREE FROM LIME, BURNING WHITE OR BUFF

4. Clay from the Greppin works near Bitterfeld.
5. Clay from Liegnitz.
6. Stoneware clay from Kottiken near Pilsen.
7. Stoneware clay from Ledez near Pilsen.

Contents.	4		5		6		7	
	Total.	Insol. in $H_2SO_4$	Total.	Insol. in $H_2SO_4$	Total.	Insol. in $H_2SO_4$	Total.	Insol. in $H_2SO_4$
Silicic acid - - -	54.99	19.07	76.12	52.04	59.42	26.67	66.76	37.12
Alumina - - -	27.91	1.36	14.51	1.30	27.12	1.03	20.94	0.58
Ferric oxide - - -	2.54		1.83		1.77		1.92	
Calcium oxide - - -	0.05		0.00		0.00		0.00	
Magnesium oxide - - -	0.83		0.66		0.52		0.81	
Potash - - -	3.67	0.15	1.83	0.14	1.50	0.09	4.64	0.27
Water - - -	9.87		4.94		9.85		4.43	

If we calculate the quartz, the other undecomposed mineral fragments and the composition of the real clay substance from the contents of alumina according to the principles laid down above, we obtain the following composition of the clays:

	4. Greppin clay. Per cent.	5. Liegnitz clay. Per cent.	6. Kottiken clay. Per cent.	7. Ledez clay. Per cent.
Quartz - - -	14.30	47.48	23.06	35.08
Feldspar and other minerals - - -	6.28	6.00	4.73	2.89
Clay substance	79.42	46.52	72.21	62.03
	100.00	100.00	100.00	100.00
The clay substance contains:	Oxygen.	Oxygen.	Oxygen.	Oxygen.
Silicic acid - - -	35.92	19.16	24.08	12.84
Alumina - - -	26.55	12.42	13.20	6.18
Ferric oxide - - -	2.54	0.76	1.83	0.55
Calcium oxide - - -	0.05	0.01	0.00	0.00
Magnesium oxide	0.83	0.33	0.66	0.26
Potash - - -	3.52	0.60	1.69	0.29
Water - - -	9.87	8.76	4.94	4.39

According to this the chemical formulas of the clays would be:

	Silicic acid.	Alumina.	Water.
4. Clay from Greppin	- 2.17	: 1	: 2.19
5. Clay from Liegnitz	- 2.49	: 1	: 1.92
6. Clay from Kottiken	- 2.14	: 1	: 2.25
7. Clay from Ledez	- - 2.28	: 1	: 1.44

For the estimation of the refractoriness of the clay substances the following numbers are obtained from the above analyses:

To one equivalent of flux there are in

4. Clay from Greppin	-	4.66 equiv. $\text{Al}_2\text{O}_3$ , and 10.19 equiv. $\text{SiO}_2$ .
5. Clay from Liegnitz	-	4.70 " " " 12.67 "
6. Clay from Kottiken	-	8.68 " " " 18.64 "
7. Clay from Ledez	-	3.20 " " " 7.32 "

In these clays, as compared with the kaolins, we notice (1) a higher content of silicic acid in the real clay substance rising to 2.5 equivalents to 1 equivalent of alumina; (2) the contents of fluxes expressed by the analysis of the whole belongs for the most part to the clay substance itself and the contents of undecomposed rock fragments is very slight as compared with the chief constituents: quartz and clay substance,—a composition which distinguishes these clays essentially, both from kaolin and from the real brick clays of which a series of analyses will be given below.

### III

#### BRICK CLAYS

8. Clay from Rathenow, washed.
9. Clinker clay from Bockhorn.
10. Clinker clay from Schwarzenhuette.
11. Clinker clay from Christiania.

The chemical analysis and the breaking up with sulphuric acid gave in the case of these clays the following results:

## 60 TREATISES OF A GENERAL SCIENTIFIC NATURE

Contents.	8		9		10		11	
	Total.	Insoluble in $H_2SO_4$ .	Total.	Insoluble in $H_2SO_4$ .	Total.	Insoluble in $H_2SO_4$ .	Total.	Insoluble in $H_2SO_4$ .
Silicic acid	61.30	35.94	70.22	53.95	77.44	63.71	61.96	39.95
Alumina . .	18.87	2.50	13.67	2.82	9.82	3.78	17.56	6.16
Oxide of Iron	6.66		6.80		5.34		6.17	
Calcium oxide	0.85		0.00		0.00		FeS .97	
Magnesium } oxide }	1.20	0.20	1.30		1.36		2.64	
Potash and } Soda }	3.30	1.23	3.37	1.35	3.87	2.32	7.18	4.68
Water . .	8.29		5.30		2.48		3.61	
	100.47	39.32	100.66	58.12	100.31	70.01	100.21	50.79

If we calculate from these results the essential mineral constituents we find :

	8	9		10		11		
Quartz -	27.17	44.06		50.64		18.33		
Feldspar and other mineral frag- ments - -	12.70	14.06		19.37		32.64		
Clay substance .	64.13	41.88		29.99		49.03		
	100.00	100.00		100.00		100.00		
The clay substance contains :		Oxygen.	Oxygen.		Oxygen.		Oxygen.	
Silicic acid -	25.36	13.52	16.27	8.67	13.73	7.32	22.01	11.74
Alumina -	16.37	7.66	11.85	5.55	6.04	2.83	11.40	5.34
Ferric oxide -	6.66	2.00	6.80	2.04	5.34	1.60	6.17	1.85
Calcium oxide -	0.85	0.24	0.00	0.00	0.00			
Magnesium oxide -	1.00	0.40	1.30	0.52	1.36	0.54	2.64	1.06
Potash and soda -	2.07	0.35	2.02	0.34	1.55	0.26	2.50	0.43
Water - -	8.29	7.36	5.30	4.71	2.48	2.20	3.61	3.21

For the clay substance there is found from this the following equivalent proportion between :

	Silicic acid.	Alumina (iron oxide).	Water (alkalies.)
Clay from Rathenow	2.09	: I : :	2.57
Clay from Bockhorn	1.71	: I : :	2.19
Clay from Osterode	2.47	: I : :	2.08
Clay from Christiania	2.45	: I : :	1.65

and the relation of the flux to silicic acid and alumina is found to be 1 equivalent of flux in the case of the

Clay from Rathenow to	3.22 equiv. of $\text{Al}_2\text{O}_3$ ,	and 6.83 equiv. of $\text{SiO}_2$ .
Clay from Bockhorn to	2.94 "	" "
Clay from Osterode to	1.85 "	" "
Clay from Christiania to	1.61 "	" "

Even if these determinations, according to the assumptions made, cannot strictly correspond to all the demands of science, they still give to practice a very good idea of the constitution of clays and make the analyses far more intelligible and applicable to practical use, than the general analyses can, especially with reference to the behavior of clays at high temperatures, without seriously increasing the work of the chemist.

We owe to the valuable contributions of Bischof and Richters our knowledge of the behavior of clays at high temperatures, and these investigators possess the honor of having made clear the importance of the individual constituents occurring in clay, in their action as fluxes as well as in their resistance to melting. The numerical expressions which Bischof gives for the degree of refractoriness of clays, according to his analysis, presupposed that all the parts indicated by the analysis take a part in the reaction occurring at the high temperatures, in the amount indicated. This, however, is by far not always the case especially with the silicic acid present in clay in the form of grains of quartz, and therefore the figures indicating the refractoriness in many cases do not give a true expression of the real resistance of clays to high temperatures. These values are least correct in the case of clays melting at a comparatively low temperature in which the presupposed chemical reactions are very slight or not present at all. At a high temperature a mass of clay does not melt evenly, but a few constituents melt first and act chemically on the more difficultly fusible particles, thus ac-

complishing the fusion of the whole. Therefore it appears of the greatest importance for the estimation of refractoriness to learn to know the greater or less fusibility of the individual constituents to be considered as chemically homogeneous, and take into consideration their relative fusibility as well as the amount. For this, the method of the chemical investigation indicated above seems far more suited than the one heretofore practiced, and if the rules set forth by Bischof are applied to the essential constituents of clays, the scientific results and practical tests will almost, if not entirely, agree. I reserve the privilege of discussing this matter again when a greater number of experiments made in this direction are at hand.

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### Contribution to the Further Knowledge of Kaolins

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PROF. CHAS. W. MESLOH, TRANSLATOR

In the numerous analyses which Forchhammer, and later Brogniart and Malaguti, have furnished of kaolins, the chief object was to shed light on the origin of clay from the feldspar or feldspathic rocks, to find out the chemical composition of kaolin clay, and trace the processes, through which the kaolin clay could develop as a final product from the weathering of feldspathic rocks. The chemical means that were employed had the purpose of simply breaking up the clay, while the other materials contained in the kaolin had to be looked upon as ballast, as confusing factors to be kept out of consideration, as far as possible in the question under discussion.

A different conception must appear when we consider kaolin from the standpoint of the manufacturer. Here those fragments of rock, which accompany the kaolin clay and which cannot be completely removed by a washing process, ever so thorough, play a very important rôle, and therefore, need a special consideration. In fact, we must ask : Whence come the differences of kaolins from various sources so far-reaching in practice if, according to the results of the above-mentioned investigation, the essential part in the kaolins, namely the clay, has in all or

nearly all cases the same composition, as we have seen in the previous chapter? Whence comes the difference in the plasticity, in shrinkage, in color, and in fusibility, etc.? We will come nearer to the solution of these questions if we try to determine the kind and amount of those bodies which accompany the kaolin clay and which enter into the composition of the products if the kaolin is used in manufacture, and to study these properties of the mass which are important for manufacturing purposes. The minerals accompanying the kaolin clay are chiefly quartz and feldspar or feldspathic minerals. Since it is hardly possible to separate the feldspar from similar silicates by analysis, we can do no more than consider them collectively as simply feldspar, an assumption certainly erroneous, but nevertheless the most practicable.

If we assume that besides kaolin clay we have to do only with quartz and feldspar, then it is possible to get nearer the constitution of kaolins and to obtain valuable information concerning their behavior in manufacturing processes and a good basis for the composition of bodies with changing raw materials. With this point in view an additional number of kaolins in the washed condition, as found in the market and used in manufacturing, were investigated with regard to their special constituents.

There are given below three kaolins from the neighborhood of Pilsen: Ledez, Kottiken and Tremosna; also the kaolins from Zettlitz, Lettin, Kaschkau, and Sennewitz; and finally the ordinary porcelain body produced from the Sennewitz kaolin in the Royal Porcelain factory at Charlottenburg.

When the bodies in question were subjected to a chemical analysis they were found to have the following composition:

	Ledes. Kaolin.	Kottiken. Kaolin.	Tremosn. Kaolin.	Zettlitz. Kaolin.	Lettin. Kaolin.	Kaschkau. Kaolin.	Sennewitz. Kaolin.	Charlottenburg porcelain body.
Silicic acid -	49.19	49.91	49.48	46.82	57.08	56.72	64.87	63.07
Alumina - -	36.73	35.99	36.34	38.49	29.94	31.07	23.83	24.67
Ferric oxide - -	0.81	0.63	0.66	1.09	0.65	0.59	0.83	0.59
Magneia - -	0.18	0.30	0.41	trace	0.49	0.22	0.50	0.40
Potash - -	1.18	0.75	1.60	1.40	2.26	0.51	1.39	4.25
Water - - -	12.41	12.34	11.99	12.86	9.87	11.18	8.36	7.00

These figures do not give a clear idea of the constitution of those kaolins and the properties that may be expected of them in manufacture. Our idea is much improved if we gain a knowledge of the composition of the real clay substance, that is, the weathering product of feldspar, and at the same time discover the nature of the unweathered, dust-like admixtures of the kaolin.

The separation of these constituents of kaolin, differing in their properties, took place in the way of the rational analysis, by breaking up the clay with concentrated sulphuric acid as described in the previous chapter. In this way we succeeded in separating the clay substance from the mineral fragments; we determined the silicic acid contained in the latter as well as the aluminum oxide or the sum of the alumina and ferric oxide.

The following little table gives the amounts of the unweathered mineral fragments, as well as their composition, in the kaolins mentioned above:

	Leder. Kaolin.	Kotiken. Kaolin.	Tremona. Kaolin.	Zettitz. Kaolin.	Lettin. Kaolin.	Kaschau. Kaolin.	Sennewitz. Kaolin.	Charlot. Barne Kaolin.
Total amount of mineral frag- ments -	11.74	12.59	9.71	3.45	25.91	21.49	36.22	45.08
Silicic acid -	9.05	10.65	7.91	3.04	23.28	21.29	35.98	38.09
Alumina -	1.70	1.21	1.09	0.21	1.73	0.11	0.14	4.15
Alkalies (by dif- ference) -	0.99	0.73	0.71	0.20	0.90	0.09	0.10	2.84

If we suppose (as previously discussed) that only quartz and feldspar are contained in the sandy residue, it is admissible to calculate the amount of feldspar from the content of alumina with the aid of the chemical formula. If now the amount of feldspar is subtracted from the total residue, the remainder gives the amount of quartz in the kaolin. We thus get in per cents the amount of quartz, feldspar, and real clay substance found in kaolin, but the composition of the clay may also be calculated without difficulty with the aid of the above analyses.

and the amount of silicic acid and alumina found in the sandy residue. The following tables give us, on the one hand, the amount of clay, quartz and feldspar in the kaolins and, on the other hand, the composition of the clay substance contained in them, in per cent, as they were found in the manner just discussed:

	Ledes. Kaolin. Per cent	Kottiken. Kaolin. Per cent	Tremosa. Kaolin. Per cent	Zettilts. Kaolin. Per cent	Lettin. Kaolin. Per cent	Kaschau. Kaolin. Per cent	Sennerville. Kaolin. Per cent	Charlottenburg body. Per cent
Clay substance	88.26	87.41	90.29	96.55	74.09	78.51	63.77	54.92
Quartz	- - -	3.08	6.40	4.08	2.30	17.21	20.90	35.50
Feldspar	- - -	8.66	6.19	5.63	1.15	8.70	0.59	0.73

Composition of the clay substance of the kaolins investigated:

Silicic acid	- -	45.36	44.76	45.98	45.36	45.63	45.00	45.30	45.46
Alumina	- - -	39.58	39.65	39.36	39.71	38.08	39.32	37.15	37.35
Ferric oxide	- -	0.92	0.72	0.73	1.13	0.88	0.75	1.29	1.07
Magnesia	- -	0.20	0.34	0.45		0.66	0.28	0.78	0.73
Potash	- -	0.21	0.02	0.99	1.24	1.84	0.53	2.02	2.57
Water	- - -	14.02	14.07	13.28	13.32	13.32	14.20	13.11	12.74

From this analysis and the figures obtained in the complete analysis we get a very clear conception of the composition of the kaolins; and on glancing at the last table we plainly see that the main portion, which gives its character to the whole, shows almost the same composition for all the varieties.

If we consider more carefully the analyses given we will see at once that the difference of the various kinds of kaolin does not really lie in the composition of the clay substance contained in them. This had also been determined by the investigations of Forchhammer, Brogniart, and Malaguti.

If in spite of this agreement in the chemical composition of a clay substance we notice very considerable differences in the properties, when a practical test is made of them, the cause for this is certainly to be found in the kind and amount of the undecomposed mineral fragments that are contained in them. And

in this regard, as is seen from the tables, very considerable differences exist. It is seen that in the case of the kaolins investigated (the porcelain body is here not considered) the content varies in the case of the clay substance from 63.77 per cent up to 96.55 per cent; quartz from 2.30 per cent up to 35.50 per cent; feldspar from 0.59 per cent up to 8.70 per cent.

These differences in the contents of those bodies must bring about essential technical differences in the behavior of the materials. In the Royal Porcelain factory, at Berlin, the kaolin from Sennewitz is used for ordinary porcelain bodies. In taking this kaolin as the basis a definite composition of the body is arrived at, in practice, which corresponds to the demands of technology in its manipulation in the unburned condition as well as for its behavior in the kiln. In the same factory kaolin from Lettin is also used for some purposes. If now instead of the kaolin from Sennewitz one wished to introduce the kaolin from Lettin empirically into the porcelain body ordinarily employed, and count on an analogous behavior of the mass, he would certainly be disappointed, as may be seen at once from the result of the analysis:

	Kaolin from Sennewitz.	Kaolin from Lettin.
Clay substance	63.77	74.09
Quartz	35.50	17.21
Feldspar	0.73	8.70

In the Royal Porcelain factory, as I learn from the kind communications of Dr. Sarnow, the porcelain body is composed of 200 parts of kaolin from Sennewitz and 60 parts of feldspar. Taking as a basis the analyses of the kaolin from Sennewitz we get the following composition of the porcelain body:

	Per cent.
Clay substance	49.50
Quartz	27.31
Feldspar	23.64

\* There were found:

	Per cent.
Clay substance	54.92
Quartz	23.52
Feldspar	21.56

These not very important deviations between the calculated and actual figures

If now instead of the kaolin from Sennewitz we should introduce the kaolin from Lettin into the body, according to the same receipt, the following figures would indicate the composition of the latter according to the analysis:

	Per cent.
Clay substance	56.99
Quartz	13.24
Feldspar	29.77

Such a body, we see, would be richer in clay and feldspar and considerably poorer in quartz. From this there would certainly result a greater plasticity in manipulation, but also greater shrinkage and greater fusibility on burning. This result, deduced from the analysis, agrees with the statements of Dr. Sarnow.

Not long ago it was debated whether the addition of quartz to the porcelain body is justifiable. Mr. Buenzli, of Eichwald, in a series of interesting articles, tried to prove, on the basis of experiments and observations, not only the justification, but even the necessity of such an addition in moderate amounts for the Bohemian porcelain which is made from the kaolin from Zettlitz. Our analyses confirm his statements to a striking degree. Buenzli says concerning the Zettlitz kaolin that it possesses considerable plasticity, and therefore would endure considerable shortening, but that it contracts and warps very much in firing. The figures, which we have found for the Zettlitz kaolin,

	Per cent.
Clay substance	96.56
Quartz	2.30
Feldspar	1.15

give a precise expression to these qualities. One can read those properties from them without ever having made a practical ex-

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of the composition of the mass may be explained from the somewhat inaccurate weighing on a large scale and the fluctuations in the hygroscopic water or perhaps also from the somewhat fluctuating constitution of the kaolin of Sennewitz, since the kaolin formerly employed for the body does not necessarily correspond to those specimens that were recently taken for investigation.

periment with the Zettlitz kaolin. Buenzli further remarks that if only feldspar to the amount of 50 or 75 per cent be added to the kaolin, we would obtain medium to very fusible spar masses, of dry biscuit surfaces, having a yellowish appearance; at the same time, however, the disagreeable qualities of warping, etc., would make themselves very much felt. But if now just as much quartz be added as there is feldspar in the mass the latter would be more stable in the fire, less dry in the biscuit surfaces, of a bluish white color and more translucent. Only when the spar acts on quartz and clay at a high temperature would transparency and glassy fracture appear and a real porcelain be formed. Spar bodies free from quartz give a drier biscuit than those containing quartz. Buenzli proves the importance of quartz for the spar body by direct experiment, by showing among other things that a rubbing on of quartz on the surface of unburned porcelain figures can serve for the production of matte, glossy biscuit figures. The cause of these phenomena is found in the fact that in the porcelain fire, feldspar possesses basic properties, and shows a supersaturation with alkali at this temperature. If no quartz is present in the body, the alkali of the spar acts on the clay, producing no vitreous mass nor luster, but a product resembling white ware. However, if quartz is present, it acts on the alkali, and the vitreous appearance characteristic of porcelain, arises. These remarks Buenzli proves in part by direct experiments. If this is accepted as true, the analysis of the Zettlitz kaolin shows the plain necessity of the addition of quartz, since in the natural condition it contains only 2.30 per cent of it, while, for example, the Sennewitz kaolin furnishes 35.50 per cent.

From these few remarks we may learn what welcome, important information the rational analysis, made from a manufacturing point of view, can give for the knowledge of the kaolins and the composition of bodies made from them. It gives a means of avoiding the uncertain empirical groping and a large number of mistakes in practical experiments, as well as disturb-

ances in the manufacture, that are produced by a change in the raw material.

Finally, for the sake of inciting others, I should like to mention a point which does not yet seem sufficiently clear; I mean the cause of the more or less strong yellow coloration of spar bodies. The differences in the content of iron determined by analysis do not seem to offer any explanation for these phenomena. The Zettlitz kaolin, for instance, shows the greatest proportion of iron, 1.09 per cent, and yet it produces beautiful white porcelain. A hint is given by the remark of Buenzli, that a spar body from this kaolin with 50 to 75 per cent of feldspar furnishes a yellow biscuit; also that the same body with the addition of just as much quartz as feldspar furnishes a biscuit of bluish white appearance. It would be important to hear the experience of practical men in this respect.

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### Notes on the Constitution of Plastic Clays

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PROFESSOR CHAS. W. MESLOH, TRANSLATOR

In the investigation concerning the constitution of kaolins we have learned to know them as mixtures of three different substances, well definable chemically; namely, quartz powder, unweathered feldspathic remains or residues of rocks similar to feldspar, and the real, pure clay substance silicate of aluminum, containing water. Only such kaolins are, of course, included here that have been freed by washing from all coarse admixtures, and are, therefore, in that condition of purity in which they may serve as a material for the production of the body for finer clay wares, especially for porcelain. This separation into three constituents, which is generally possible, and of which clay substance, always of the same composition, is by far the most predominant, is important for the reason that the same

substances which appear as the companions of clay substance must be artificially added to it in the production of bodies. From the constitution of kaolin (namely, its greater or less content of quartz and feldspar) the change in its properties may be explained, and it is clear, therefore, that for the composition of bodies we must constantly regard the amounts of quartz and feldspar naturally contained in the kaolin material.

What holds good for the constitution of the kaolins may likewise be taken as true in the case of the other clays, except that with these, in consequence of the washing process that always preceded the deposition, many impurities have gotten into it whose nature is often very hard to determine on account of the very close incorporation.

Above all, if a similar constitution of kaolins and plastic clays is assumed, there remains to be determined, what difference there is in the clay substance, so different in its properties in the kaolins and plastic clays, and whether this physical difference can be explained chemically. The clay substance of the kaolins differs very much in its properties from that of the real plastic clays. That of the former is short and from a plastic dough dries out to a loose, dusty mass, while that of the latter contracts more in drying to a dense, hard, horny, brittle substance. These differences are of great influence on the use that is made of it and the necessary manipulations.

In order to solve this question, of course, only such clays could be used which can be compared with the kaolins with reference to their purity and their freedom from chance admixtures; and since the use in manufacture gives a good hint in this regard only such clays were compared that serve as raw materials for the manufacture of white ware and stoneware.

The following analyses were in part prepared in the technical chemical laboratory for the clay industry, and in part were made specially for this investigation.

The analyses refer to the following clays:

- I. A lean white clay for stoneware, of French origin,  
source not mentioned.

- II. Unctuous clay of the same source.
- III.
- IV. } White-ware clays which are used in a large German factory, source not indicated.
- V. }
- VI.
- VII. White clay from Ebernhahn near Coblenz.
- VIII. White clay from Baumbach near Coblenz.
- IX. White clay from Bendorf near Coblenz.
- X. White clay from Laemmersbach near Coblenz.
- XI. White clay from Hoehr near Coblenz.
- XII. Yellow clay, burning red, from Moschheim near Coblenz.

The clays mentioned under VII to XII are the ones chiefly used in Nassau.

The chemical analysis of these clays gave the following figures in which it must be noted that the alkalis are not separated, but always calculated as potash; the decomposition of the clay substance or its separation from quartz and feldspathic remains, was accomplished by heating with strong sulphuric acid:

	I.	II.	III.	IV.	V.	VI.
	Total. Insoluble in H <sub>2</sub> SO <sub>4</sub> .	Insoluble Total. in H <sub>2</sub> SO <sub>4</sub> .				
Silicic acid -	-75.35	54.84	60.49	62.16	65.89	63.11
Alumina -	- 16.60	0.62	26.10	0.51	26.12	0.49
Ferric oxide -	- 1.09	trace	2.11	0.99	0.71	1.04
Calcium oxide -	- 0.53	trace	0.56	0.39	0.37	0.32
Magnesia -	- 1.55	trace	1.03	0.70	0.48	1.02
Potash -	- 4.80	trace	9.80	9.92	10.27	10.17
Loss on heating -	-	100.14	100.28	100.28	99.90	100.49
	99.92					100.25

	VII.	VIII.	IX.	X.	XI.	XII.
	Total. Insoluble in H <sub>2</sub> SO <sub>4</sub> .	Insoluble Total. in H <sub>2</sub> SO <sub>4</sub> .				
Silicic acid -	- 60.76	27.56	59.28	78.22	64.53	33.14
Alumina -	- 26.84	1.05	28.63	9.24	0.63	0.48
Ferric oxide -	- 0.99	trace	1.29	0.47	1.01	0.77
Calcium oxide -	- 0.52	0.61	0.35	trace	0.34	0.39
Magnesia -	- 3.65	3.44	2.11	3.06	2.62	1.27
Potash -	- 7.26	7.39	3.78	6.55	4.92	3.65
Loss on ignition -	-	100.02	100.02	100.02	100.02	100.02

The striking absence of lime in nearly all the clays investigated allows us to infer, with some degree of probability, that we have to do here with pure weathering products of clay-forming rocks without noteworthy foreign admixtures. If now as in former analyses we consider the alumina contained in the part not decomposed by sulphuric acid, as belonging to the undecomposed feldspathic remains, and subtract from the silicic acid the part which corresponds to the content of alumina as being the silicic acid of the feldspar (3.51 per cent of silicic acid to 1 per cent of alumina), the rest remains as the quartz content of the clay. From these calculations the clays showed themselves as mixtures of:

	I.	II.	III.	IV.	V.	VI.
Clay substance -	44.63	71.54	68.82	61.48	67.80	79.47
Quartz - -	52.77	25.97	29.06	37.48	30.41	18.92
Feldspathic re- mains - }	2.60	2.49	2.12	1.04	1.89	1.61
	VII.	VIII.	IX.	X.	XI.	XII.
Clay substance -	71.22	76.30	39.71	66.23	54.73	78.07
Quartz - -	24.03	22.40	57.15	31.42	41.77	19.75
Feldspathic re- mains - }	4.75	1.30	3.14	2.35	3.50	2.18

We see from these figures that all the clays possess only small amounts of undecomposed feldspathic mineral fragments, and that they show themselves essentially as mixtures of clay substance and quartz powder.

This calculation of the analyses allows us to investigate the materials from a uniform standpoint and explains the differences of the properties by fluctuations in the amount of admixed quartz powder and the degree of its distribution; we obtain a better conception of the peculiarities of the clays if we calculate the composition of the clay substance from the results of the analyses by subtracting from these figures the amounts of silicic acid,

alumina, and potash corresponding to the quartz and feldspar contents and dividing the rest into 100 parts.

From these calculations we obtain the following figures as the percentage composition of the clay substance or rather of that part of the clay decomposed by sulphuric acid:

	I.	II.	III.	IV.	V.	VI.
Silicic acid -	45.99	45.75	45.67	44.27	46.16	46.52
Alumina -	38.08	35.77	37.42	35.58	36.17	38.55
Iron oxide -	2.44	2.94	1.44	1.15	1.55	1.01
Calcium oxide -	trace					
Magnesia -	1.19	0.78	0.57	0.60	0.48	0.34
Potash -	2.36	1.24	0.39	0.45	0.97	0.56
Loss on heating -	10.76	13.70	14.41	16.67	15.93	14.32
	VII.	VIII.	IX.	X.	XI.	XII.
Silicic acid -	46.62	47.44	47.44	47.39	47.45	42.06
Alumina -	36.01	37.21	35.74	36.40	37.88	28.06
Iron oxide -	1.39	1.68	1.94	1.52	1.41	14.62
Calcium oxide -	trace		trace			trace
Magnesia -	0.73	0.79	0.88	0.51	0.71	1.62
Potash -	3.47	4.22	3.85	3.96	4.08	4.02
Loss on heating -	10.19	9.69	9.52	9.92	9.00	9.03

What is especially surprising in these figures is their very close agreement, which shows that the assumptions made are correct, and that the clays which in part come from places far distant from one another, nevertheless have almost the same composition in their clay substance.

We find an exception only in the very ferruginous clay of Moschheim, which, however, is easily explained; apparently we have to deal here with a clay which, as a high content of oxide of iron shows, does not owe its origin to a clay-forming rock, but to ferruginous minerals, or to a rock in which a deposition of hydrate of iron has taken place by the subsequent infiltration of ferruginous waters.

These results give interesting information also in an-

other respect. Essential differences in them are found only in the content of alkalis and water. On comparing figures we find that those clay substances which show a high proportion of alkali show a small proportion of water, while those in which the content of alkali almost completely vanishes, show a much larger proportion of water; hence we might be justified in concluding that these can mutually displace each other.

A high proportion of alkali causes the clays to become dense more readily by vitrification; the content of water brings about greater porosity after burning and increases greatly the difficulty of vitrification already great on account of the small proportion of alkali; and in fact the experiments made show that the clays III to VI, poor in alkali, are to be counted with the refractory ones, while the clays VII to XII possess only a slight degree of refractoriness. Furthermore, it is worthy of note that the composition of the clay substance in the clays VII to XI, which come from sources lying close together, show a surprising constancy, and the differences in their composition are to be sought solely in the greater or less content of finely divided quartz.

If in conclusion we compare the composition of the clay substance of the investigated plastic clays with that of kaolin which was given in the previous essay, we find also in this a wonderful agreement.

If from the analyses given in the previous chapter we calculate the average of the composition of the clay substance of the seven kaolins, we get the following figures:

	Per cent.
Silicic acid -	45.34
Alumina -	38.98
Iron oxide -	0.92
Calcium oxide -	<hr/>
Magnesia -	0.52
Potash -	0.98
Water -	13.62

The above figures show such a great family resemblance to

others given in this chapter that, aside from the greater proportion of alkali found in the plastic clays, which, moreover, is also subject to fluctuations in the kaolin, we cannot find an essential chemical difference, and it is clear that as with the kaolins so also with the purer plastic clays the differences in their behavior in firing are to be looked for in the fluctuations in the amount of alkali and water contained in the clay substance.

Concerning the very prominent differences in the degree of plasticity, which in the case of the kaolins is reduced to a minimum, even with those having a much higher content of pure aluminum silicate, the chemical composition gives us no explanation. The degree of plasticity, therefore, does not seem peculiar to a definite chemical combination; but seems to vary according to the degree of mechanical division and the kind of the molecular arrangement in substances having the same chemical composition. It is perhaps to be explained from the structure of the rocks to which clay owes its origin.

These investigations now show, in the most decisive manner, that it is not sufficient to know the composition of the clay as a whole in order to make conclusions in regard to its properties and deduce its usefulness for certain technical purposes, but that we must go back to the mineralogically different parts, and especially to the composition of the part most prominent quantitatively—the clay substance—which gives to the material its character in most cases.

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### The Orsat Apparatus

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PROFESSOR CHAS. W. MESLOH, TRANSLATOR

It is known that a certain volume of air is necessary for the advantageous combustion of a fuel and that if this is not maintained the combustion will not take place economically, or as is often the case in the operations of the clay industries, the products of combustion will have an injurious effect on the wares.

The chemical process which we call combustion and which we use to develop the higher temperatures for our purposes, is brought about by putting compounds rich in carbon, of a vegetable or mineral origin (wood, peat, lignite, bituminous coal, anthracite, etc.), into a condition in which their constituents, essentially their carbon and hydrogen, enter into a chemical reaction with the atmospheric oxygen. The atmospheric air consists in round numbers of 79 parts by volume of nitrogen, and 21 parts by volume of oxygen, of which the former, however, takes no part in the combustion, but rather helps to lessen the heat effect produced by the combustion, because it is carried off through the chimney, for the most part, heated to a high degree, together with the products of combustion. The greatest amount of heat is developed when the oxygen just suffices to burn the carbon of the fuel to carbonic acid and its hydrogen to water, when the relation of the fuel to the air is such that to six parts by weight of the carbon of the former there are supplied 16 parts by weight of oxygen and to one part by weight of hydrogen there are supplied eight parts by weight of oxygen. If the air is present in a greater proportion the surplus air supplied plays the same rôle as the nitrogen, that is, introduces losses of heat; if a smaller proportion is supplied, combustible products (carbon monoxide, hydrogen, tar vapors, soot) would escape with the smoke, causing a direct loss of fuel. Whether or not the latter takes place in the combustion, the fireman, in most cases, will see from the appearance of the flame, which is then usually red and lacks luster; the products of combustion appearing more or less colored. On the other hand, it is more difficult to tell whether the air is supplied in excess.

In all rational furnaces, we must aim at making the products of combustion consist only of nitrogen, carbon dioxide and water vapor, and reduce the excess of oxygen as well as the carbon monoxide to a minimum.

Only by chemical analysis is it possible to determine definitely whether the air supplied by the draft of the chimney or

fan, is just sufficient for combustion. Heretofore this could be done only in the chemical laboratory and formed one of the most difficult problems for chemists, since it required very subtle apparatus and a large number of precautionary measures, so that the hand of a skilful experimenter was always needed. The chemical analysis of fire gases has therefore been of use in extremely few cases. In most branches of industry chemistry has created methods which permit also the non-technical to make investigations of raw materials and products in a short time and to control the course of the industrial processes. I will mention here only the use of the aerometer for soluble substances, methods of titration for the determination of alkalies, iron, copper, lead, zinc, in the ores, the polarization apparatus for sugar, and others; for the most important process in the whole field of industry there was heretofore no method by means of which it might be examined by an untrained person.

We are very fortunate in having an apparatus with the help of which we can examine the fire gases in a few minutes and regulate the supply of air according to the result. The apparatus does not need the hand of the chemist for its manipulation but may be worked by any intelligent skilful workman. It was originated by Orsat, a Frenchman, and described in a pamphlet on the use of gaseous fuel for industrial purposes by the French engineer, A. Fichet, in Paris. To be sure, the apparatus does not give the accurate results which would be required for scientific purposes and is limited to the determination of the chief constituents of the fire gases, carbon dioxide, oxygen, carbon monoxide and nitrogen, but it possesses sufficient accuracy for practical purposes.

In using the apparatus a certain amount of gas is drawn from the furnace, gradually exposed to caustic soda distributed over a large surface, then to sodium pyrogallate and finally to an ammoniacal solution of cuprous chloride. The first one removes the carbon dioxide, the second the oxygen, the third is a solvent for the carbon monoxide, leaving only the nitrogen.

If 100 cc. of the fire gases are measured and the decrease in volume noted, after a treatment with the various absorbing liquids, the percentages of the individual constituents are obtained directly, without calculation, by the decrease in volume, expressed in cubic centimeters. The improved apparatus is constructed as follows:

The measuring burette A, of 100 cc. capacity, is surrounded by a large cylinder filled with water, in order to protect the gas from changes of temperature. The lower 45 cc. are divided into tenths of a cubic centimeter, the upper 55 cc. into cubic centimeters. More than 40 per cent of carbon dioxide, carbon monoxide and oxygen will hardly appear even in a blast-furnace gas, hence all determinations can be carefully read to tenths of a per cent. A thick-walled capillary tube, carrying the stop-cock, is firmly supported near the top of the frame. This capillary tube is bent at the left end and connected with a U tube B, whose arms contain cotton while water is placed in the lower part to keep all soot and dust out and to saturate the gas with moisture before it is measured; the end of the cock c, directed to the rear, is connected by a rubber tube with a rubber aspirator, C, by means of which we can easily fill the supply tube and B with the fire gases to be examined. The absorption takes place in the U-shaped vessels D, E, and F, which are connected by short rubber tubes with the stop-cock and filled with glass tubes to increase the absorbing surface. The other end of the U tubes are closed with rubber stoppers

Fig. 1.

that contain the little glass tubes X; the small tubes are connected with rubber bulbs to keep out the atmospheric oxygen.

On using the apparatus the cylinder surrounding the burette A, as well as the bottle L, is first filled with distilled water. For filling the three absorbing bottles we take off the stoppers containing the glass tubes X, and the rubber bulbs, and pour into the vessel D about 100 cc. of caustic potash having a specific gravity of 1.26 to 1.28 so that the vessel is a little more than half-filled with it. Furthermore, we dissolve 18 grams of pyrogallic acid in about 40 grams of hot water, add 70 cc. of caustic potash, and run the mixture into the second vessel E, for absorbing oxygen. To determine the carbon monoxide we put 35 grams of cuprous chloride with 200 cc. of hydrochloric acid and about 50 grams of copper clippings into a tightly closed bottle, allow it to stand a day with frequent shaking, and add 120 cc. of water in order to fill the vessel F with the solution obtained. The cock c is placed in the horizontal position and the bottle L raised so that the water will run into the burette A. The cock is turned so that the opening leads to the tube B and vessel D and then the flask L is lowered. The pinch-cock on the tube S is carefully opened so that the caustic potash can rise to the mark M whereupon the cock is closed. In a similar way the liquids of the other two vessels are raised to the mark M, while the eye is constantly directed to the rising liquid (it is best to practice this operation first with pure water). The three stoppers with the glass tubes X are then placed on air-tight. Into the tubes B we now put about 1 cc. of water, fill both arms with loose cotton, replace the stopper and connect the second arm of B by means of a stopper, glass tube and rubber tube, with the iron or porcelain tube which is placed air-tight into the flue to prevent the entrance of atmospheric air.

In order to find out whether the apparatus is air-tight, the cock c is placed in the horizontal position, the rubber tube attached to the tube in the flue is closed by means of a pinch-cock

or the hand, and the pinch-cock of the tube S opened. The column of water in A sinks somewhat, but must then remain stationary, since a continued slow sinking would indicate a leak somewhere which must first be removed either by better fastening of the rubber tubes, deeper insertion of the corks or greasing the glass cocks with vaseline.

After the burette A has been filled with water by raising the bottle L, to the mark 100, the cock c is so placed that a connection is produced through the tube B, from the aspirator C, with the flue. Now by pressing C ten or fifteen times a suction is produced which fills the whole passage with the gas to be examined. This is done most conveniently by pressing the aspirator C, repeatedly, ten to twenty times according to the length of the connecting tube. The cock c is again placed in the horizontal position, the pinch-cock of S is opened, and the bottle L lowered until the burette A is filled to the zero mark with the fire gases to be analyzed, whereupon c is closed again by a quarter of a turn to the left. The gas is now enclosed between the glass cocks and the column of water in A.

For the determination of the carbon dioxide the cock of D is opened, L raised with the left hand so that on opening the pinch-cock of S with the right hand the gas passes over into the tube D; L is now lowered again until the caustic potash in D reaches the connection of the tube below M, and the gas is driven once more into the vessel containing the caustic potash by raising L. By lowering the bottle L, and carefully opening the pinch-cock the caustic potash is made to rise to the mark M. The stop-cock is closed, the pinch-cock opened, the bottle L held to the side of the burette so that the water in both vessels stands equally high; the pinch-cock is again closed and the volume of the gas remaining is noted. The position of the water-level gives directly the percentage of carbon dioxide contained in the gas examined. In a similar way the gas is made to pass two or three times into the vessel E until there is no longer a decrease in volume; the reading at this point gives the amount of carbon dioxide and oxygen together, while by a similar treat-

ment of the gas in the vessel F, the carbon monoxide is also absorbed.

The gas which now remains in A is nitrogen. We have, therefore, the amount of the four gases that were to be determined.

When the analysis is finished the cock c is again placed in the horizontal position, L raised, the pinch-cock opened and the water made to rise in the burette up to 100 cc.; the cock c is again placed vertically, the connecting passage is filled with the gas to be examined and a new sample taken. If, as usual, there is no carbon monoxide present an analysis may be made every four or five minutes, with a little practice, correct to 1/5 per cent. If the absorption is slow after 100 to 200 analyses the vessels are emptied by means of a small siphon, washed with distilled water and filled again with caustic potash, pyrogallate, and cuprous chloride.

If through carelessness the absorbing liquids should rise into the capillary tube, the bottle L, is raised, the pinch-cock opened and the solution washed back into the vessel by means of distilled water. If this is not altogether successful, the rubber tube connecting with C, is removed, and water made to run through the capillary tube until it is perfectly clean. If in this way impurities were added to the water in the burette, it must be renewed.

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### Investigation of Fire Gases in the Continuous Lime Kiln with Orsat's Apparatus

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PROF. CHAS. W. MESLOH, TRANSLATOR

The introduction of Orsat's apparatus, announced in a pamphlet by A. Fichet, on gas firing, made it possible to carry out with little trouble a large series of investigations on the composition of waste gases and thus to note the course of the fire. Even

though the determinations made by means of the Orsat apparatus lack extreme scientific accuracy, the information obtained thereby is accurate enough for practical purposes, and this method of investigation has the advantage over more accurate methods, that the results are obtained within a few minutes, and the fire can be regulated accordingly.

Schinz states that to obtain complete combustion with grate firing, it is necessary to supply double the amount of air necessary for the combustion of the fuel, according to the chemical composition, so that half of the oxygen of the air passing through the grate is not used.

It seemed interesting to investigate (1) what the relation is between air and fuel in the continuous kiln? (2) what influence an abundant supply of coal has on the composition of the fire gases? and (3) what differences appear in the composition of the products of combustion at the floor immediately under the arch at the place of maximum heat, and in the neighborhood of the damper?

Atmospheric air consists in round numbers of 79 parts by volume of nitrogen and 21 parts by volume of oxygen with fractions of a per cent of carbon dioxide and water vapor, which may, however, be neglected, since they are not important for our consideration. In the products of combustion, carbon dioxide and water vapor take the place of the oxygen if the combustion was complete, of which the former occupies the same volume as the oxygen that was used for its formation; if the combustion was incomplete carbon monoxide is present which occupies double the space of the oxygen that is used for its formation; besides water vapor, hydrogen and hydrocarbon compounds are formed if the temperature was not high enough and if the oxygen was present in insufficient amounts for complete combustion. Nitrogen, on the other hand, is altogether indifferent in all cases, and therefore its amount in the products of combustion furnishes a very good means of calculating the amount of air<sup>1</sup> which has passed

<sup>1</sup> If O designates the amount of oxygen which is still present in the products of

the fire without having been deprived of its oxygen. Besides the results of the investigation there is given in the following tables in a special column the percentage of air, found by calculation, which was actually used in the combustion.

The carbon dioxide which is present in the combustion gases of a lime kiln arises either from the combustion of the coal used in the heating or is evolved from the limestone by the influence of the heat produced. The proportion of each may be determined by calculation, as the composition of the coal is known and that of the fire gases. The calculation<sup>1</sup> of the relation between the carbon dioxide coming from the fuel and that from

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combustion, then the amount of nitrogen ( $\pi$ ) which corresponds to it to give with it such a mixture as is present in the atmospheric air, is  $\frac{79}{21} \times O$ . If  $N$  designates the whole amount of nitrogen found in the fire gases, we calculate the amount which belongs to the air that has actually been burnt and deprived of its oxygen, by  $\pi = N - \pi = N - \frac{79}{21} \times O$ , or expressed in per cents,

$$N : N - \frac{79}{21} \times O = 100 : a, \text{ or } a = \frac{100 (N - \frac{79}{21} \times O)}{N}.$$

If, for instance, in the products of combustion the amount of oxygen still found be 4 per cent, that of nitrogen 73 per cent, then the amount of air which was actually deprived of its oxygen is equal to

$$x = \frac{100 (73 - \frac{79}{21} \times 4)}{73} = \frac{100 \times 58}{73} = 79 \text{ per cent};$$

that is, of the whole amount of air entering the furnace 79 per cent has been used and 21 per cent has gone through without exercising any effect.

<sup>1</sup> If atmospheric air was used for the complete combustion of pure carbon the final result is 79 per cent of nitrogen and 21 per cent of carbon dioxide; if, however, the coal contains hydrogen as is always the case, excepting in the use of coke or charcoal, then a part of the oxygen is used for the combustion of the hydrogen and the amount of carbon dioxide is correspondingly reduced.

In this special case the carbon content of the coal was 34.88 per cent, that of the combustible hydrogen 1.87 per cent. One part by weight of hydrogen requires eight parts by weight of oxygen, and six parts by weight of carbon, sixteen parts by weight of oxygen for complete combustion. 1.87 parts by weight of hydrogen accordingly  $1.87 \times 8$  of oxygen = 14.96, and 34.88 parts by weight of carbon  $34.88 \times \frac{16}{6} = 93.02$  parts by weight, therefore, for 100 parts by weight of carbon 107.98 parts by weight of oxygen.

Of the 21 parts of oxygen which is contained in the air there were used in the combustion of the carbon  $\frac{21 \times 93.02}{107.89} = 18.1$  parts by volume, for the combustion of the hydrogen  $\frac{21 \times 14.96}{107.89} = 2.9$  parts by volume.

Since every part by volume of oxygen on combustion furnishes again one part

the limestone has been carried out everywhere and has been added to the results of the investigation.

The following series of experiments was carried out by Dr. Aron and myself with the continuous lime kiln of Frederick Hoffman in Berlin in such a manner that with two apparatus, fire gases were taken at the same time from the bottom of the furnace and from under the arch. The gas was taken by boring two holes through a cover and inserting air-tight, two wrought iron gas tubes  $\frac{1}{4}$  of an inch in diameter, of which the one ended 10 cm. from the bottom of the kiln, the other 10 cm. from the top. Each of these tubes was connected to the Orsat apparatus by means of a rubber tube. To prevent the action of the metallic iron on the gases of combustion the tubes, before being placed into the furnace, were washed out with a hot solution of boric acid and a glassy lining was produced on the inner surface.

Together with the analysis of the fire gases carried out at intervals of ten to twenty minutes simultaneously above and below in the kiln, the strength of the draft was measured and registered.

The kiln was fired in every case by filling 4 or 5 rows of holes, that is, 12 to 15 shafts according to the strength of the

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by volume of carbon dioxide, the carbon dioxide and nitrogen are in the proportion of 18.1 : 79, assuming the same composition of coal as above.

Since now the amount of nitrogen which corresponds to that part of the air that has lost its oxygen by combustion, may be deduced from the experiment, there is given also the amount of carbon dioxide which corresponds to the oxygen which has disappeared.

If the percentage of air used in combustion is indicated by  $a$ , the nitrogen found in the fire gas by  $N$ , then the amount of nitrogen which belongs to the oxygen, which has vanished, is equal to  $\frac{N \times a}{100}$ . For the calculation of the corresponding amounts of carbon dioxide the proportion, therefore, is  $79 : 18.1 = \frac{N \times a}{100} : x$ ;  $x = \frac{N \times a \times 18.1}{100 \times 79}$ .

If, for example, the amount of nitrogen was found be 69 per cent and the percentage of air consumed had been calculated as 95 from the oxygen content, then there would correspond to the oxygen vanished, a carbon dioxide content of  $\frac{69 \times 65 \times 18.1}{100 \times 79} = 15.06$  per cent of the fire gases. If now on examination a larger content of carbon dioxide is found, as for instance, 30 per cent (in the test No. 48) the difference of 15 per cent represents the amount of carbon dioxide that has been driven out of the limestone.

draft, with lignite up to the top of the arch, at intervals of one to one and a half hours, and awaiting the complete ignition and settling to the level of the flues built in the limestone above the floor of the kiln, before putting in the next charge.

The fire gas was always taken from the low red part of the kiln; the place is always indicated in the tables as well as the place where the instrument for measuring the draft was attached.

The furnace was fired with a very moist earthy lignite of low calorific power. It contained:

	Per cent.
Carbon	34.88
Hydrogen	3.81
Oxygen	15.53
Moisture	42.69
Ash	3.09

Besides the carbon there was consumed 1.87 per cent of hydrogen while the remainder, 1.94 per cent, corresponds to the oxygen content of the coal used for the formation of water. The theoretical fuel value of the coal deduced from the analysis is 2950 calories.

In this experiment the fire had been kept for some time in one place since a progression was not advisable on account of the neighborhood of the damper. By a previous pause in the burning the temperature had sunk very low; consequently the combustion was slow. The evolution of the carbon dioxide from the limestone reduced almost to zero, in consequence of the previous long firing at one place and the low temperature of the furnace.

The second series of tests shows the composition of the fire gases with a slow progression of the fire so that the daily capacity of one chamber was not fully realized; the gas was taken at different distances from the full fire and with varying draft.

From this table we see in the clearest manner the influence of the firing on the composition of the gases as well as the distribution of the products of combustion and their chemical composition at various heights in the kiln. We see that with the

beginning of firing with coal, the oxygen content of the fire gases decreases till it reaches its minimum at the end of the charging and the carbon dioxide its maximum, and with the burning down of the coal a gradual rise in the excess of air supply appears. The percentage of oxygen actually burned is quite high and rises to over 80 per cent, falling to below 50 per cent just before a new charge of coal. These differences seem quite large, yet they are small as compared with grate firing, for in the case of the latter we notice in most cases the appearance of reducing gases (that is, a lack of the necessary oxygen for complete combustion) by the colored smoke which rises from the chimney immediately after firing, while the content of excess oxygen in the burning down of the fire is probably, in most cases, greater. The composition of the fire gases is almost the same near, as at a distance from, the full fire, above and below in the kiln. That, in consequence of this uniform combustion at various places of the furnace, a uniform temperature is developed, is seen from the fact that the evolution of carbon dioxide from the limestone is uniform near the kiln floor and below the arch.

With an increased draft, however, in the kiln, as we see from the last section of the series of experiments, the percentage of the unused air becomes greater under the arch; this is still more marked in the third series of experiments. This may be caused by the fact that with the increased draft, the products of combustion must take a more horizontal path and cannot rise from the lower parts of the kiln; or in consequence of the more rapid sinking of the fuel in the firing flues the coal goes out of the upper shafts sooner than out of the lower ones, and that therefore the fire gases can pass under the arch without sufficiently coming in contact with the glowing coal. With a stronger draft, as we shall see, the amount of carbon dioxide evolved from the limestone diminishes. This does not agree at all with the assumption formerly made in which a strong draft increases the formation of carbon dioxide, but seems capable of being explained by the fact that through the increase of an excess of air a slight

First Series of Tests. FOUR ROWS OF FIRE HOLES AT FULL HEAT

nm.	Section of section	Carbon dioxide derived from										Remarks.					
		Composition of fire gases 10 cm. above kiln floor.										Carbon dioxide derived from					
		Limestone		Chlorite		Oxygenn.		Carbon monoxide		Air made available		Limestone		Coal		Per cent.	
		Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
1	11 25	56														2.5	6.0
2	11 40	56														1.0	11.0
3	11 50	53														0.5	12.0
4	12 5	55														0.5	10.0
5	12 20	55	10.0	9.5	0.0	80.5	56.0	0.0	10.0	9.0	11.5	0.0	80.5	46.0	0.5	8.5	While burning down
6	12 35	55	10.0	10.0	0.0	80.0	53.0	0.5	9.5	10.0	9.5	0.0	80.5	56.0	0.0	10.0	" "
7	12 50	53	7.0	12.5	0.0	80.5	42.0	0.0	7.5	8.5	11.0	0.0	80.5	49.0	0.0	8.5	" "
8	1 25	53	4.0	16.0	0.0	80.0	25.0	0.0	4.0	9.5	12.0	0.0	79.5	43.0	1.5	8.0	Just before firing
9	1 45	53	7.0	13.0	0.0	80.0	39.0	0.0	7.0	9.5	11.0	0.0	79.5	48.0	1.5	8.0	During firing
10	1 55	53	7.5	12.5	0.0	80.5	42.0	0.0	7.5	9.0	10.5	0.0	80.5	51.0	0.0	9.0	During firing

## **INVESTIGATION OF FIRE GASES**

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**SECOND SERIES. FOUR ROWS AT FULL HEAT. a**

SECOND SERIES. FOUR ROWS AT FULL HEAT. b.—Continued

Time of ob- servation. Hrs. Min. utes	Number.	Gas taken from 6th hole in front of full fire. Drawn measured at 17th hole before full heat.		Remarks as to place of sampling.				Section of stack. mm.		Composition of fire gases 10 cm. below crown.		Composition of fire gases 10 cm. above kiln floor.		Carbon dioxide derived from		Remarks.		
		Oxygen.	Dioxide.	Nitrogen.	Carbon dioxide.	Nitrogen.	Carbon dioxide.	Nitrogen.	Carbon dioxide.	Nitrogen.	Carbon dioxide.	Nitrogen.	Carbon dioxide.	Nitrogen.	Carbon dioxide.	Nitrogen.	Carbon dioxide.	Nitrogen.
26	1	10	22	15.0	9.5	0.0	75.5	53	6.0	9.0	13.5	10.5	0.0	76.0	48	5.0	8.5	While burning down
27	1	20	37	9.5	13.5	0.0	77.0	34	3.5	6.0	8.0	15.0	0.0	77.0	27	3.0	5.0	While burning down
28	3	15	66	8.5	13.5	0.0	78.0	35	2.0	6.5	11.0	12.5	0.0	76.5	39	4.0	7.0	While burning down
29	3	30	70	10.0	11.0	0.0	79.0	48	1.5	8.5	12.0	—	—	—	—	—	—	During firing
30	3	40	75	17.0	4.0	0.0	79.0	81	2.5	14.5	17.0	5.5	0.0	77.5	76	3.5	13.5	At end of firing
31	3	50	70	13.5	7.5	0.0	79.0	64	2.0	11.5	14.5	7.0	0.0	78.5	66	2.5	12.0	While burning down
32	4	10	70	12.0	9.5	0.0	78.5	54	2.5	9.5	13.5	7.5	0.0	79.0	64	2.0	11.5	While burning down
33	4	30	70	9.5	12.0	0.0	78.5	43	1.5	8.0	11.0	10.0	0.0	79.0	52	1.5	9.5	While burning down
34	4	45	66	8.0	14.0	0.0	78.0	33	2.0	6.0	10.0	11.5	0.0	78.5	45	2.0	8.0	While burning down
35	5	65	10.5	12.0	0.0	77.5	43	3.0	7.5	14.5	10.0	0.0	75.5	50	6.0	8.5	Beginning of firing	
36	5	15	67	11.5	10.5	0.0	78.0	49	2.5	9.0	14.5	10.0	0.0	76.5	52	5.0	9.0	During firing
37	5	30	65	10.0	12.0	0.0	78.0	42	2.5	7.5	14.0	10.0	0.0	76.5	52	5.0	9.0	—

## INVESTIGATION OF FIRE GASES

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THIRD SERIES. FIVE ROWS IN FIRE. *a*

THIRD SERIES. FIVE ROWS IN FIRE. b.—Continued

## **INVESTIGATION OF FIRE GASES**

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FOURTH SERIES

lowering of the temperature has been produced, so that the evolution of carbon dioxide has been somewhat decreased. Even if we assume that the evolution of carbon dioxide is not diminished, the percentage would still be less since the amount of gases drawn in by the kiln has become greater.

The third series shows the continuous kiln in a condition in which it possesses so high a temperature and the fire progresses in such a lively manner that the production exceeds the normal one by one chamber daily.

In this case it is more evident than previously that a strong draft produces inequalities in the composition of the gases that become greater with an increase of draft. While in all cases the composition of the gases on the floor of the kiln is subjected to slight fluctuations and theoretically shows the most favorable condition for the development of a very high temperature, the differences become very great under the arch.

From this we can explain the phenomenon that with a very strong draft the highest heat is developed at the bottom of the kiln while under the arch it decreases so much at times that it falls below the degree necessary for burning wares to a matured condition; that is, the phenomenon appears which the burners call "not being able to hold the fire."

On increasing the number of holes fired, the phenomenon is shown that immediately after the firing, carbon monoxide appears at the bottom of the kiln; that, therefore, the oxygen is not sufficient for the combustion, while under the arch it is present in excess. The last determinations, however, furnish the proof that the carbon monoxide does not get to the chimney but that in the low red chambers a sufficient mixture of the gases containing oxygen above and carbon monoxide below takes place to make the combustion a complete one.

Still more plainly than from the preceding tables, the influence of the draft on the composition of the fire gases in regard to their absolute content of excess of oxygen, as well as to the amount of carbon dioxide evolved from the fuel and the limestone, and the amount of air passing through indifferently, ap-

pears from the last table which, excluding the fluctuations that are caused by the supply of fuel in large amounts, shows only the average composition with a given draft and temperature from the time of one charge to the other.

From these average values it is clearly shown that with a moderate draft the composition of the gases at various heights in the kiln is almost the same; hence uniform conditions exist for the generation of heat and the evolution of carbon dioxide as far as this is possible with the natural irregularities. With a stronger draft, however, judging from the air excess considerable differences are shown between top and bottom. If we look at the figures which, other things being equal, express the amounts of carbon dioxide derived from the coal and the limestone, we note on the one hand that, as was to be expected, with a rising temperature in the kiln the amount of carbon dioxide developed from the limestone increases both absolutely and relatively as compared with the amount coming from the coal, and that therefore a high temperature makes possible not only a more rapid burning, but that also the heating effect of the coal must be considerably higher than at a temperature which just suffices to free the carbon dioxide from the limestone, and, on the other hand, that the proportion of the carbon dioxide coming from the two sources remains the same above and below.

This seems to indicate that the assumption frequently made that a large amount of carbon dioxide in the fire gas retards the decomposition of the calcium carbonate and that the evolution of carbon dioxide is all the more vigorous the greater the movement of the air, is not true in the measure generally assumed. With a very strong draft it appears evident, from the tests made and especially for the upper portions of the kiln, that the very large amount of air is not in a correct, but in an unfavorable, proportion to the fuel. Through this disproportion the temperature necessary for the decomposition is not reached, and we see from the first series of tests that even with a strong draft there

is no evolution of carbon dioxide if the requisite temperature is not attained. If a larger amount of carbon dioxide in the fire gases appears in the lower parts of the kiln in general (and especially with a strong draft) than under the arch, this arises from the fact that the amount of air which passes the cross-section of the kiln at its bottom, is under these circumstances smaller than that passing through the upper regions of the kiln. The carbon dioxide evolved is therefore less diluted by atmospheric air passing uselessly through the kiln.

The assumption frequently made, that the heavy gases, here the carbon dioxide, are especially inclined to pass through the lower parts of the kiln, a statement which has often appeared in the discussions of the general conventions of the German Society for the manufacture of brick, clayware, lime, and cement, and to which an especial importance has been given, is not correct from other reasons of a purely physical nature and so shows itself here; where an especially large amount of carbon dioxide appears at the bottom of the kiln, it may be explained, from the experiments made, by the fact that the movement of the fire gases in the lower parts of the kiln is slower, on account of the greater resistance by friction with a strong draft, than above and that below the carbon dioxide evolved is less diluted by the atmospheric air passing through indifferently without chemical effect.

At any rate it may be seen that however desirable a strong circulation of air must undoubtedly be in the manufacture of lime, in order to burn in a given time a definite quantity of coal corresponding to the lime to be burned, for the greatest and most intense effect, the velocity of the draft must not exceed a certain limit. The quantity of the air will be all the greater, and in consequence, the progress of the fire can be hastened all the more, the more rapidly coal may be changed into gaseous products. In every special case the dimensions of the kiln, the size of the rock, the manner of charging, and necessary degree of heat, can exercise an influence in this direction if one wishes to obtain as nearly as possible theoretical results.

## The Investigation of Industrial Gases

PROF. CHAS. W. MESLOH, TRANSLATOR

The demands which are made on methods for the investigation of gases, if they are to serve technical purposes, must be essentially different from those which are made exclusively for scientific purposes. In the latter the highest obtainable degree of accuracy is demanded, while with the former, above all, rapidity of execution is necessary in order to be able to follow, step by step, the technical process with the accuracy limited to a certain degree.

Orsat's apparatus, much used recently for investigations of this kind, answers the latter requirement, but permits a direct determination of only a part of the constituents of the fire gases, namely, carbon dioxide, oxygen, and carbon monoxide, while for the kilns of the clay industries the determination of other constituents, especially of hydrogen and hydrocarbons, seems of importance. Orsat's apparatus, lately modified by him in such a manner that also the determination of the last-named substances is made possible, seemed unsuited for the purpose at hand, because it is too complicated and the sources of error far exceed the permissible amount, so that its readings lose their value.

The advantage which Orsat's apparatus has, that it does not make necessary work in a laboratory but may be set up by the side of the kiln, could not decide in favor of its choice; for the sake of greater accuracy the determinations, according to the method to be described later, were made in the laboratory.

Samples for the investigation were taken in the following manner: At the place in the kiln at which samples of the combustion gases are to be taken, a porcelain tube, of about 1 cm. inside diameter, and 1.25-1.35 mm. long, is firmly walled in so that the one end is accessible from without and may be kept closed by means of a cork.

For aspirating the kiln gases a suction flask containing 5

liters is used; this is filled with water which is covered with a layer of rapeseed oil, 1 cm. thick, to prevent the immediate contact of the gases of combustion with the water. This suction

flask, *A*, has in its rubber stopper a glass-cock, *a*, and a tube, *b*, reaching almost to the bottom, which is connected on the outside by means of a rubber tube with a straight tube sufficiently long to cause the complete removal of the water through the siphon. The bottle, *A*, is placed upon a small wooden bench. The connecting rubber tube may be closed by means of a pinch-cock supplied with a screw which at the same time serves to regulate the flow.

Fig. 2.

Before taking a sample the suction

flask is so filled, by means of the siphon from a higher vessel, that no air bubbles remain in it and the cock, *a*, is filled with oil up to its orifice. The cock, *a*, is then connected by means of a rubber tube with the porcelain tube walled into the kiln after the air in the passageway has been removed by suction with the mouth, and fire gases have taken its place. By opening the cock, *a*, we cause the water to flow out and regulate the flow by means of the pinch-cock so that the suction flask is filled in about fifteen minutes with fire gases (about 5 liters). The samples of gas taken from the kiln as an average of the composition during the time indicated are now transferred to smaller vessels, sufficient for the investigation to be transported in them and to be preserved until the time of determination. These vessels, *B*, have the form given in the cut, hold about 300 cc. and are supplied at their orifices with a short rubber tube, one end of which may be closed by means of a glass rod, the other by means of a pinch-cock with a screw. They are filled by connecting the opening provided with the pinch-cock by means of a tube, *a*, with a suction flask and by elevating the vessel, *A*, and lowering

the suction flask, *A*, thus again filling the latter with water and driving the gas through the cock into the small vessel. The gas will gradually drive out the air contained in the vessels. Not until the sample is removed from the suction flask, excepting a small amount, are the openings of the vessel, *B*, closed tightly. In this way we are able to take samples in a short time at any number of places in the kiln, simultaneously in about twenty or twenty-five minutes, and to keep them for future investigation.

To determine those constituents of a fire gas which can be removed by absorbing liquids, namely, carbon dioxide, oxygen, and carbon monoxide taken up in caustic soda, pyrogallic acid and cuprous chloride, we use an apparatus, *C*, agreeing essentially with Bunte's gas burette. With reference to later manipulation some changes have to be made in order to avoid calculations. The burette, *C*, with which, with some practice, we can work just as rapidly as with Orsat's apparatus, and which is cheaper, besides giving more reliable and accurate results, consists of a cylindrical vessel for measuring, *d*, enlarged in its upper part, containing about 100 cc., whose lower contracted part of about 30 cc. is supplied with a scale showing divisions of tenths of cubic centimeters. The zero point of the scale lies about 5 cm. above the lower cock; from here on the burette contains exactly 100 cc.

The burette may be closed below by a cock, *f*, which runs out to a point, and above by a three-way cock, *g*, which permits of communication with the external air through its point as well as with a spherical vessel, *e*, for washing, that holds from 50 to 60 cc. The three-way cock, *g*, is set directly on the measuring vessel without the capillary connecting piece used in Bunte's burette. The vessel for washing, *e*, has no mark, because the measurements are carried out under atmospheric pressure owing to later determinations in the eudiometer. For equalizing the pressure in the measuring vessel with the atmospheric pressure, a cylindrical tube, *k*, which may be moved in a perpendicular direction, is attached to the burette stand; this ends



Fig. 3.

100 TREATISES OF A GENERAL SCIENTIFIC NATURE

in a capillary rubber tube that can be closed by means of a clamp. This tube can be attached to the point of the cock /

Fig. 4.

whereby a communicating tube is produced. The burette is fastened in an arm capable of turning in the socket ; so that a shaking of the gases contained in it, is made possible by an oscillating movement of the absorption liquid.

In order to get the sample of gas to be investigated into the burette, the latter is first completely filled with water. This is done from the elevated large glass vessel *A*, having a hole at the bottom, communicating with the long rubber tube *I* provided with a clamp; this tube is pushed upon the point of the open cock *f*. The air escapes through the three-way cock open to the outside. Thereupon the vessel *B*, containing the sample of gas, is placed into a cylinder filled with water; the glass rod closing it below, is removed under water and a small capillary rubber tube fastened at the other end by means of a little glass tube. After opening the clamp, 20 to 25 cc. of the gas are first allowed to escape in order to crowd out the air contained in the tube, which is then placed upon the horizontal point of the cock *g*, and the water allowed to flow out of the cock *f*. When the burette is entirely filled with gas and the cocks are closed again, the volume must be brought to 100 cc. This is done by causing so much water to flow through the cock *f* from the vessel *A*, that its level stands at the zero point of the scale. The gas in the burette now, of course, has a higher tension than the external atmosphere; to equalize the pressure it is only necessary to open the cock *g*, outwardly to cause the excess to flow out.

In order to convey the absorbing liquids into the burette we proceed in the way proposed by Bunte. The liquid is removed through the cock *f* by means of a suction flask and in its place the reagents contained in a small beaker are made to rise: for the determination of carbon dioxide, caustic soda (1:7); for the determination of the oxygen, pyrogallic acid and caustic soda; for the determination of carbon monoxide,<sup>1</sup> an ammoniacal solution of saturated cuprous chloride (prepared as described in the chapter on the Orsat apparatus). After introducing the reagents the absorption is brought about by the oscillating movement of the burette about its center of rotation, *i*, lasting one to two minutes.

Before reading the losses in volume produced by the absorb-

<sup>1</sup> The errors in the determination of the carbon monoxide that may be produced by the presence of ammonia, amount from 0.5 to 1.0 cc.

ing liquids a removal of the same is absolutely necessary, because they differ very much in regard to adhesion to the glass. For this purpose the cock, *g*, is first so placed that water flows from the washing vessel, *e*, into the burette. By opening the cock, *f*, the absorbing liquid flows out without any loss of gas while the water, which flows in from *e*, washes the sides of the burette and at the same time gives to the volume of gas the temperature of the water and removes the ammoniacal gas which gained access through the absorption of the carbon monoxide.

After closing the cock the pressure is equalized by connecting the lower cock, *f*, with the communicating tube, *k*; the liquids are then brought to the same level and the reading taken. In connecting the rubber tube with the point of the lower cock, care must be taken that no air bubbles are found in it; water must be allowed to flow out freely before the tube is put on.

For the removal of the reagents used and the wash-water, a large glass funnel is sunk into the table under the burette stand communicating with a pot placed below.

The determination of the hydrogen and the hydrocarbons contained after the absorption in the remainder of the gas, is made in the simplest way by exploding in a eudiometer after the addition of some oxygen or electrolytic hydrogen, using a water-seal.<sup>1</sup> The eudiometer, *D*, is about 50 cm. long, holds about 130 cc., and has platinum wires melted in at the upper end; it is also provided with a scale showing tenths of cubic centimeters. In the upper end the eudiometer tube is protected against heating by a cork shell, 8 cm. long and 1 cm. thick. To transfer the remainder of the gas from the burette into the eudiometer a rubber tube, ending in a curved glass tube, is connected with the point of the cock, *g*, and first filled with water by causing it to flow from the washing vessel, *e*, through the tube into the water receptacle of the eudiometer till no more air bubbles arise. Then

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<sup>1</sup> It is to be recommended to use in place of the ordinary cylindrical eudiometers such as are widened in their upper part like the burettes of the Bunte gas burette and the new Orsat apparatus. They can thus be made shorter and handier, and also provided with a more distinct calibration scale.

the glass end of the tube is placed under the mouth of the eudiometer filled with water, and from the vessel, *A*, water is made to flow through the cock, *f*, into the burette, which forces the gas, without any loss, into the eudiometer through the three-way cock turned in the opposite direction.

Thereupon oxygen is made to enter the eudiometer (5 to 10 cc. in the case of fire gases, 20 to 30 cc. in the case of generator gases). The oxygen is kept on hand in a large bottle or flask, *E*, which is arranged exactly like the suction flask, *A*, used to take the sample. The oxygen contained in it, which suffices for several hundred analyses after one filling, is always kept under pressure by elevating the vessel, *E*. The delivery tube, which may be closed by means of a glass cock, empties into the trough of the eudiometer below the surface of the water. After the entrance of the oxygen the volume is measured by lowering the eudiometer into the glass cylinder, *F*, which is about 60 cm. high, filled with water, and the reading is taken with the water within and without at the same level.

The removal of the eudiometer from the bath into the glass cylinder does not take place by closing it with the thumb, but in the simplest, surest, and most rapid way by placing under the opening a little long-handled mustard spoon of porcelain or glass.

In the investigation of fire gases the gas mixture contained in the eudiometer after the addition of the oxygen is never explosive; an addition of electrolytic hydrogen gas, which must likewise be constantly kept on hand, is necessary.

The hydrogen gas is evolved by the apparatus, *G*, according to the principle of Doeberreiner, under whose bell the platinum electrodes end in well insulated wires. The current from a battery of six Leclanche cells is sufficient to furnish the hydrogen gas even with very rapid work.

In analyses of fire gases an addition of from 25 to 35 cc. is required, while in those of generator gases little or nothing. The exit tube of the hydrogen reservoir ends under water in the bath of the eudiometer. After the introduction of oxygen and hydrogen respectively, the latter not being measured, the explosion of the

gas mixture is accomplished by means of an electric spark through the platinum wires of the eudiometer. The latter is placed upon a rubber plate, weighted by a piece of lead, and is pressed against the rubber by being fastened to a strong arm of the stand. The rubber plate, of course, is placed at the bottom of the eudiometer bath. For igniting the gas mixture there was first used a small Leyden jar, according to Bunsen's specification, which is charged by rubbing a porcelain tube with a silk cloth; but for convenience and rapidity this was replaced by a small induction apparatus, using a battery as the source of electricity, zinc-carbon in chromic acid.

After the explosion has taken place, which is recognized by a sharp sound, the eudiometer is immediately released and, after the water column rises, is placed into the cylinder *F*, 60 cm. high and filled with water for the purpose of cooling, being completely immersed in the water. After five minutes the decrease in volume caused by the combustion of the hydrogen and hydrocarbons can be read, the eudiometer being raised so that the interior and exterior water-levels are the same.

There remains still the determination of carbon dioxide produced by the combustion of the hydrocarbons. This is done by means of absorption in caustic soda in the eudiometer itself. For introducing the reagent there is used the small glass cylinder *H*, and a test-tube narrowed by heating over the Bunsen burner and drawing out, and which is fitted air-tight into a rubber stopper fitting in the opening of the eudiometer. The test-tube is filled with strong soda-lye and lowered into the cylinder *H*, so that the water in the latter stands about 3 to 4 cm. above the upper edge. On account of its higher specific gravity the caustic soda remains in the vessel. The eudiometer is now, as previously explained, lifted into the cylinder by means of a mustard spoon, placed over the small tube under water, at the same time being pressed over the rubber stopper and thus closed at the lower end. It can then be taken out and shaken so that the caustic soda is mixed with the water in the eudiometer and the carbon dioxide absorbed. The opening of the eudi-

ometer is again placed under the water-level of the cylinder *H*, the rubber stopper and the tube removed by means of crucible tongs, and the eudiometer lowered with the help of the mustard spoon into a second, high cylinder, *J*, for the purpose of cooling. On making a reading of the volume of gas still remaining, the eudiometer being raised until the interior and exterior water-levels are the same, the quantity of carbon dioxide produced by the combustion of the hydrocarbons is obtained.

By means of the loss in volume caused by the explosion in the eudiometer (the hydrogen added not being considered) and the contents of carbon dioxide absorbed by the caustic soda, the factors for the calculation of the hydrocarbons, ethylene,  $C_2H_4$ , and marsh gas, methane,  $CH_4$ , are given and the calculation can be done mentally. To the chemist this is self-evident ; for the benefit of the non-chemist it may be said that one volume of ethylene causes a contraction of two volumes on exploding and that the products of combustion furnish two volumes of carbon dioxide ; the marsh gas likewise causes a contraction of two volumes, but produces only one part by volume of carbon dioxide ; hydrogen, on burning, contracts one and one-half volumes.

However complicated the method may at first seem to be, on account of the large number of pieces of apparatus, very quick work may be done with it. At the same time it gives very accurate results. The influence of varying temperature during the experiment is completely removed by the use of water which is kept constantly at hand in a larger reservoir of about 30 liters as a washing and cooling liquid ; the barometric pressure may be left out of consideration, since an analysis does not require half an hour. The gases investigated are always saturated with water-vapor at the time of reading, and the readings are taken only with water used as seal, so that possible errors on account of differences in the adhesion of liquids are excluded ; the ammoniacal gas measured with the carbon monoxide in Orsat's apparatus and the ordinary burette by Bunte, is here removed and the absorption of gases by the water is reduced as much as

possible by using only water which has stood for several days in the room. As a consequence, analyses of the same sample show no greater differences in the individual constituents than 0.1 per cent. The absorption analyses in the burette do not require any more time than with Orsat's apparatus, with greater accuracy of results, namely, about fifteen minutes. The work with the eudiometer requires about as much time. With some practice and correct division of the work it is possible to work with both apparatus at the same time so that two analyses may be made at once. It is thus possible, if an assistant takes the samples from the kiln, to carry out eighteen to twenty complete analyses of the fire gases or generator gases in one day.

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### Some Investigations Pertaining to the Colors of Brick

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The clay substance in its purest form as kaolin has a white appearance, and all phenomena of coloring that we observe in clays are caused by impurities. In this respect iron and its compounds are especially to be considered; among the raw materials used for the manufacture of clay wares there is hardly a single one which is absolutely free from iron; with ordinary clays its compounds often appear in very large amounts. The only other coloring constituent of clay which might be considered here is manganese; it is always accompanied by iron, but compared with iron is found in such small amounts that its coloring power is only rarely shown.

The intensity with which iron appears in its coloring properties depends not only on the amount in which it is present, but also on the stage or degree of oxidation in which it is found, and a large number of physical and chemical conditions of the clay, so that almost an infinite series of color relations may be caused by it. In practice the material must be very carefully treated in the case of the highly colored clays to pro-

duce an approximate uniformity of color in the products manufactured.

If we observe the gradations of color which appear in iron oxide itself, the combination with which we have to do in most cases in the coloring of clay wares, the extremely great variety of color phenomena which it produces, will be clear.

The color tint assumed by chemically pure ferric oxide, varies very much, according to its density and its mode of preparation; thus the preparation obtained from ferric nitrate is brownish red, that from iron sulphate, on slight ignition, red with a tinge into orange. However it may have been produced, on strong heating and consequent increase in density the color of the iron oxide becomes invariably darker, and this increases rapidly with the temperature. At an intense white heat it turns to blackish brown or dark violet. In general, the coloration of clay products by iron oxide becomes the darker, the higher the temperature to which they are exposed.

Outside of the quantity and degree of density in which the iron exists in the clay, under the influence of the burning, the greater or less degree of porosity is of influence in regard to the color tint. We know that colored bodies in a dense condition always possess a darker color than when they occur in a finely divided condition, that is, in the form of powder, when between their molecules there are thin envelopes of air, a condition which exists in the pores of all clays not burned to vitrification.

Of further influence upon the color is also the chemical condition in which the coloring iron oxide is present in the clay, whether it is mixed with the latter mechanically, or whether it has already entered into combination with some of the constituents. In the latter case there will be found other physical phenomena and other colorations. While the iron oxide by itself always possesses a shade of red or brown, glasses and slags colored due to the presence of smaller quantities of iron oxide are colorless or yellow, while they have a yellowish brown or brown color with a higher content of iron oxide and show tints such as the free oxide never assumes.

Although we might assume that all those clays, which consist only of the real colorless clay substance and admixed iron-bearing mineral detritus, or their weathering products, or free iron oxide, or the hydroxide of the latter, always assume a shade of brown or red after burning (the colors of pure iron oxide diluted by colorless ingredients to a lower intensity), entirely different color phenomena are produced if there are substances present in the clay which may cause deep-seated chemical, as well as physical, changes during the burning. We observe this, for instance, when brick clays contain considerable amounts of calcium carbonate. In this case the red color produced by the iron at a lower temperature disappears at the vitrification temperature sometimes entirely, and is only noticed unpleasantly in connection with faulty water smoking and burning. Not only the lime (and perhaps also the magnesia where the latter is present in larger quantity) but also the content of alumina in the material, seem to act in a similar way as will be discussed later on under the head of materials high in alumina.

Outside of the ferric oxide there comes into consideration also the iron compound, lower in oxygen, in regard to the coloration of clays; this lower oxide is formed during the burning from the higher, in presence of carbonaceous substances in the clay or under the influence of fire gases, or at a very high temperature. It may also have been originally present in the clay. On the whole, it is a much stronger coloring agent than the ferric oxide.

It is known from the glass industry that the iron in the form of ferrous oxide, colors the glass a very intense green or black, and that decoloration of the glass, or with much impurity a lightening of the color, takes place if the lower oxide is changed to the higher by the addition of oxidizing substances, as manganese, saltpeter, and arsenic acid. The color which the ferrous oxide gives to clay is green, violet, or black, according to the absolute amount and the relative proportion between the two stages of the oxidization of iron; in general, therefore, at least with porous ware, the development of the

ferrous oxide is never desired on account of its intense coloring power and its instability, and is a normal constituent only in the production of highly vitrified products—the clinkers.

If we wish to classify the clays according to the colors which the mass assumes on burning without considering the accidental colors or surface colors produced unintentionally, we can divide them into four groups:

1. Clays high in alumina and low in iron. These burn white or to a scarcely noticeable color.

2. Clays high in alumina containing moderate amounts of iron; their color ranges from pale yellow to buff.

3. Clays low in alumina and high in iron, the brick clays, burning red.

4. Clays low in alumina, high in iron and lime, the brick clays burning yellow, or clay marl.

i. To the first group of clays belong the raw materials for the finest products of the clay industry, the kaolins or porcelain earths, as well as a number of plastic clays. Even, though we speak of the porcelain earths in consequence of their pure white color as being free from iron compounds, this is never found true on chemical analysis.

Bruno Kerl, in his well-known work "Abriss der Thonwaaren-Industrie," gives a large series of analyses of kaolins and porcelains which show that the amount of iron, very small in many cases, often exceeds 1 per cent without seriously affecting the whiteness of the body. To mention a few examples the amount of ferric oxide in the porcelain of Nymphenburg was found to be 2.5 per cent; in the Berlin porcelain, 0.6 to 1.74 per cent; in the Meissen porcelain, 0.8 per cent; in porcelain from China, 1.2 per cent; from Limoges, 0.7 per cent. Even if this amount of iron seems very small as compared with the common clays it still appears very strange that with the normal treatment of the porcelain the colors vary so little that only a trained eye can detect any coloring at all. The presence of large amounts of alumina (and we have to do in this case with clays containing

the largest amount of alumina) probably has a similar effect on the color of the ferric oxide as the presence of large amounts of lime in the clays; a phenomenon to be discussed later on seems to indicate, with reference to the coloration of the clay of the second group, that a large proportion of alumina is able to destroy the color of the ferric oxide. Besides the porcelain earths, a number of plastic clays might be included in this group, which, in burning, take a pure white color, and are used for the manufacture of clay pipes and fine faience ware.

2. To the second group belong those clays which burn white at a low heat, sometimes with a pinkish tint, but at higher temperatures take on a more or less yellowish or brownish color, however, never a reddish color nor one changing to green at high temperatures. This group comprises the majority of the so-called plastic clays or the fire clays in all stages of refractoriness down to the lignite clays used only for the manufacture of bricks. As a rule these possess a comparatively large amount of alumina, 20 to 30 per cent, and over, at the same time an amount of iron which approximates in some cases that of the red burning brick clays, but in most cases is far below it (1 to 5 per cent). These, as also the clays of the first group, claim the interest of the brick-maker in a less degree than the clays of the third and fourth group, because they are not fitted for the production of bricks on account of their high refractoriness; they are chiefly used for the finer branches of ceramics and for the manufacture of chamotte brick. Only the least refractory clays of this group are used for the production of bricks and terra cotta, as for instance the yellow burning clays from the lignite beds of the Lausitz (Greppin, Siegersdorf, and Bunzlau clays). It seems as though in these clays the large amount of alumina destroys the red shade of ferric oxide as lime does in other clays and changes it to a yellow or yellowish brown; this is evident from the fact that a mixture of the red burning clay of the third group and white burning clay of the first group does not produce pale red brick in consequence of the dilution of the red material by the white, but that the red passes over into a

yellow or brown. As an example of such a mixture I may mention the well-known buff brick which was used as front brick in rebuilding the bank building in Berlin.

A number of analyses of materials which belong to the class of the yellow or brown burning clays just discussed, low in lime, give an idea of the relation in which the coloring ferric oxide stands to the others, the non-coloring constituents, and leads to interesting considerations, especially if we compare the proportions of iron oxide in the various specimens with each other, and also with the analogous figures found from analyses of red burning clays given later.

Clay from	Poole (England). Per cent.	Senften- berg. Per cent.	Neuwied. Per cent.	Neuwied. Per cent.	Schoene- beck. Per cent.
Silicic acid - - -	59.61	62.50	56.05	64.37	75.38
Alumina - - -	26.81	21.30	25.05	21.91	15.01
Ferric oxide - - -	2.03	3.06	4.68	3.04	2.39
Calcium oxide - - -	0.82	0.58	0.97	0.70	0.80
Magnesia - - -	0.44	0.53	1.23	1.37	
Potash - - - -	2.77	2.18 }	2.46	2.99	2.38
Soda - - - -	0.80	0.81 }			
Chemically bound water } and organic substances }	7.46	8.57	9.10	4.71	4.84
Color after burning } (hard burn) }	white to yellow- ish white	light buff	yellow to buff	yellow- ish bro'n	yellow
Proportion of ferric oxide and alumina - -	1:13.2	1:7.0	1:5.4	1:7.2	1:6.3

From the analyses we see that from the absolute quantity of the coloring substance no reliable conclusion can be drawn in regard to the color that the clay takes after burning; a large number of physical and chemical conditions which now escape observation play a part in the coloration; the above-mentioned clays have in common, however, that they all show a shade of color which varies from white or yellowish white to brown, according to the temperature to which they were exposed.

With regard to the color phenomena which they show, these

clays have a great similarity to the clays of the fourth group (those rich in iron and lime), but are distinguished from the latter by their great refractoriness. They are to be classified with the refractory clays, or at least very near them, and in passing over into the dense porcelain-like condition they never assume the green color characteristic of lime clays, but generally a brown or gray color.

In the above representatives of clays of the second group it is seen that the content of alumina by far exceeds the content of ferric oxide, and that the relations by weight in the examples mentioned varies between 1 : 5.4 and 1 : 13. From this we deduce, with some degree of probability, assuming like temperatures and like porosity, that the clays of this group will burn all the lighter the less, absolutely and relatively, the content of ferric oxide in them is as compared with the amount of alumina.

3. The third group of clays is formed by the red burning clays, the most important and in general also the most weather-resistant brick materials. They show a smaller amount of alumina and generally a larger amount of iron than the materials of the preceding group; for this reason they are, on the whole, more easily fusible. The proportion of lime, magnesia, and alkalies is, as a rule, only small with the clays taking an intense color. On burning, the color is first a pale red which, with greater heat and increasing density of the mass, passes over into an intense red, later on into a violet-red, and finally into a bluish black.

The analyses of clays (page 113) which show the color phenomena of this group in a characteristic way, admit of a comparison with the clays in the previous table.

We see that in these pronounced red burning clays, the proportion of ferric oxide to alumina has become a very different one from that of the preceding group and the amount of ferric oxide is only one-half or one-third as large as the amount of alumina. However slight the qualitative differences are in the analyses of clays of the second and third group, and how little the constituents, to be considered as fluxes, vary, both groups

are still completely characterized by the relation between the ferric oxide and alumina.

Clay from	Rathenow (washed).	Bock- horn <sup>1</sup> .	Schwarze- huette <sup>2</sup> .	Ottweiler.	Ulm.
Silicic acid - - -	61.30	70.22	79.43	68.34	56.33
Alumina - - -	18.87	13.67	10.07	16.25	22.37
Ferric oxide - - -	6.66	6.80	5.35	5.63	7.64
Calcium oxide - - -	0.85		FeOo.12		1.46
Magnesia - - -	1.20	1.30	1.40	1.49	1.86
Potash }			2.36}		
Soda }	3.20	3.37	1.62}	3.79	2.22
Water - - -	8.28	5.30		4.32	8.10
Color after burning } (hard burn) -	dark red	dark red to violet	dark cherry-red	dark red	dark red
Proportion of ferric oxide to alumina -	1:2.8	1:2.0	1:1.9	1:2.9	1:2.9

Those in which the amount of alumina is not more than three times the amount of ferric oxide, show a decided red color; those in which the amount of alumina is five and a half times and more larger than the amount of ferric oxide possess a decided brown or yellow color; to be sure there are still other factors, such as the temperature of firing, the porosity, or vitrification of the clay, which will, however, change the limits but little since they probably only bring about a change in the shade of the one or the other color.

Between the red and yellow burning clays there is a large series of intermediate stages that correspond to a proportion of ferric oxide and alumina in which the latter is large enough to modify the red color, but not sufficiently large to bring about a pronounced yellow color. There arises from this a large series of mixed colors which cannot be used for the purpose of face brick and terra cotta in which a pronounced pure shade or color is especially desired.

4. The fourth group which contains clays of no less importance than the previous one, comprises the materials high in cal-

<sup>1</sup> Material of the famous Oldenburg paving brick.

<sup>2</sup> Analyzed in the burned condition.

cium carbonate, often to be designated as clay marls. They have a special interest for the brickmaker, because they are much more sensitive in regard to coloration and more difficult of treatment than the foregoing, since differences in color, with them, make themselves felt in a much higher degree in burning.

With the clays high in lime the color phenomena appear in an inverse order from those appearing in the clays burning yellow or red; while with the latter the color becomes darker and darker with increased temperature, with the clay marls the red color of the iron oxide appears first at a low temperature; at a higher temperature, when the lime begins to act chemically on the silicates of the clay, the red color diminishes and passes through flesh color into white or yellowish white; on more advanced vitrification the color becomes yellowish green or green and on complete melting passes over into dark green or black.

In all other clays, the coloration is produced by the iron oxide whose red color is, however, modified by the presence of lime with the formation of silicates of iron and lime that have a yellow or white color; under what circumstances such an influence makes itself felt has been discussed elsewhere.<sup>1</sup>

The following analyses give an idea of the composition of such brick materials that contain lime and burn yellow.

We see from the figures that the absolute amount of iron is almost as large as that in the clays burning red, and also that the ratio of the iron oxide to the alumina corresponds to that of the previous group; in fact all these brick materials will give a red color on weak burning.

The general assumption, therefore, that the amount of iron contained in the yellow burning marls is smaller than in the case of the red burning clays because the bricks made from them frequently take on an almost white color, is not at all justified and is not the case with the marls given above, to be considered as types of such materials, although possible in some cases on account of the great differences in composition.

Prof. Remmelé has pointed out that the yellow color is due

<sup>1</sup> Notizblatt, 1872, No. 4.

Clay from	'Velten.	Stettin.	Neuhof.	Sczegedin.	Birkenwerder.	Labyazyn.
Silicic acid -	47.86	55.79	55.02	56.07	48.34	46.67
Alumina, -	11.90	9.29	13.90	14.02	11.63	13.06
Ferric oxide,	5.18	5.79	4.53	5.49	4.59	5.31
Calcium oxide, -	14.96	18.78	10.95	16.53	15.87	11.46
Magnesia, -	1.71	2.10	1.76	0.69	1.79	4.08
Potash, -	2.65					3.33
Soda, -	1.01		1.48		2.78	0.70
Carbon dioxide,				8.64		
Water and organic substance}	10.44				11.71	10.40
Color after burning, -	4.64		3.31		5.28	4.30
Ratio of ferric oxide to alumina,	1:2.3	1:1.6	1:3.1	1:2.5	1:2.5	1:2.4
Ratio of ferric oxide to calcium oxide,	1:2.9	1:3.2	1:2.2	1:3.0	1:3.5	1:2.2

{ soft burn : red to flesh color ; hard burn : yellowish white to sulphur-yellow ; vitrification : yellowish green to green.

altogether to the presence of a large amount of lime which enters into a yellow or yellowish white combination with the other elements of the clay when vitrification begins; it was left undecided, however, what proportion of lime was required, compared with the other constituents especially oxide of iron, in order to change the red color of the latter into yellow.

In the analyses given above the ratio of the iron oxide to lime varies between 1:2 and 1:3. We may assume, however, since the materials investigated show the yellow coloration in a very characteristic way, that the proportion of lime can decrease still more without losing entirely its effect on the iron oxide.

An attempt has been made to solve this question synthetically. The red burning Rathenow clay, whose analysis is given above, was mixed with pure calcium carbonate obtained by precipitating from calcium chloride in different proportions so that for one part of iron oxide 1, 2, 3, up to 8 parts of calcium carbonate were added. Taking into consideration the small amount of lime contained in the clay, the ratio of the iron oxide to the lime in the samples was as follows :

Experiment	0	1	2	3	4
	1:0.13	1:0.48	1:0.83	1:1.18	1:1.53
Experiment	5	6	7	8	
	1:1.88	1:2.23	1:2.58	1:2.93	

These nine samples in the form of slabs, 10 cm. long and 1.5 cm. thick were exposed to a moderate red heat in a muffle, surrounded by flame, in a kiln heated with illuminating gas so that all were subjected to the action of the heat under the same conditions; after cooling all the samples were found to be colored red without any considerable difference in shade. The samples were then exposed to a higher temperature, a bright red heat. After cooling, quite different phenomena appeared; they had all passed into the condition which in brick-making is called hard burning. The colors of the samples 0, 1, 2, 3 had remained red but had taken on a disagreeable shade proportionate to the lime which they contain; four showed a yellowish brown layer about 1 mm. thick, but still colored red in the interior; in 5 and 6 the yellow layer became thicker while the fracture of samples 7 and 8 was found to be quite yellow, on breaking, with a grayish cast. From this we can see that the yellow coloration appears first and most readily with the mixtures high in lime, and also that a proportion of 1 : 1.5 between ferric oxide and lime (in sample 4) seems sufficient to produce a yellow color at a temperature sufficiently high and continued long enough.

In all the analyses given above the lime content is much higher than this proportion.

The true yellow burning clays are followed by those in which the proportion of lime is not large enough to produce the yellow color. With these appears, however, the phenomenon which is characteristic of calcareous clays, namely, that with increasing heat the red color pales more and more, while with the real red burning clays it becomes darker under the same conditions.

In the foregoing remarks we had in mind, on the one hand only the phenomenon of color which the materials show in the body and on the surface as far as this color corresponds with

that of the fracture; on the other hand only those which may be referred to the effect of the ferric oxide. In the above analyses, therefore, the iron has always been given as ferric oxide.

Surface colors as they are produced by the efflorescence of salts during the process of drying, by the action of fire gases and water vapors during the water-smoking process, by the deposition of dust and alkali vapors, may for the present be left unconsidered as chance phenomena or such as may be explained by irrational management. It remains, therefore, to explain those phenomena which are caused by the influence of the lower oxidation of iron, the ferrous oxide.

Not only among brick-makers, but also among chemists, the view is generally held that the red color of burned clays is to be ascribed to ferric oxide, the yellow color, on the other hand, to the presence of ferrous oxide, and that, therefore, in burning, red bricks can be produced in those parts of the kiln where there is an abundant supply of air, or if in cooling, air can get at the red hot bricks.

Prof. Remmelé has already proved<sup>1</sup> that in two brick clays, examined in the laboratory of the Mining Academy,<sup>2</sup> which contained in the raw condition large amounts of ferrous oxide, and of which the one burns red and the other yellow, nevertheless, after burning, the iron existed only in the ferric state.

From this he draws the conclusion that the ferrous oxide is no longer a normal constituent of porous burned products, but is always changed into ferric oxide on heating, and that in the one case the yellow color was to be ascribed solely to the large amount of lime present. At the last general meeting of the German Society for the Manufacture of Bricks, etc., Mr. Mendheim brought forth the claim that in burning bricks with gas the yellow brick became red in those parts of the kiln where an oxidizing flame prevails, and remain yellow in a neutral and reducing flame. This has led me to investigate this matter more

<sup>1</sup> Remarks Concerning the Condition of Oxidization of Iron and Some Reactions of Brick Kilns, *Notizblatt*, (1868), p. 173.

<sup>2</sup> *Notizblatt*, (1867), p. 119.

closely, and to examine a series of red and yellow bricks, both containing lime and free from lime with regard to the amount of ferrous oxide contained in them, and I must confirm the results of Prof. Remmelé, with the limitation that I have found ferrous oxide in all cases in such small amounts, that an essential influence upon coloration cannot be ascribed to it, and also that the amount of protoxide may be quite large in porous bricks without causing any noticeable difference in the color, while with porcelain-like vitrified bricks, free from pores, the color changes appear in a more pronounced degree. Among the determinations of ferrous oxide, those need especially to be emphasized in which different colors appear in one brick, where it must be assumed, therefore, that slight variations in chemical composition are the cause of the differences in color.

I shall classify the determinations of the ferrous oxide in the same way as was done with the color phenomena of the ferric oxide, and afterwards deduce the conclusions to be drawn from them.

Group I. White clays—none.

Group II. Clays burning yellow to brown, high in alumina, low in lime :

	Ferric oxide. Per cent.	Ferrous oxide. Per cent.
Bricks from Senftenberg, yellow, - - -	3.28	0.14
Bricks from Senftenberg, yellowish white,	3.29	0.42

Group III. Clays burning red :

	Ferric oxide. Per cent.	Ferrous oxide. Per cent.
Rathenow building brick, - - - - -	7.07	0.18
Clinkers from Schwarzehuette :		
Dark cherry-red, - - - - -	5.35	0.12
Dark greenish gray, - - - - -	3.43	1.85
Dark violet, - - - - -	2.14	3.01

Group IV. Clays burning yellow to green containing much lime:

	Ferric oxide Per cent.	Ferrous oxide. Per cent.	Sulphuric acid. Per cent.
Birkenwerder, yellow face brick, - - -	5.26	0.16	
Velten, yellow stove tiles, - - - -	4.84	1.17	
Brick from Neuhof, white reddish, - -	3.18	1.19	
Brick from Neuhof, yellowish green, - -	2.01	2.85	
Brick, Hungarian size, origin unknown—pale red and yellowish green:			
Red portion, - - - - -	—	0.33	
Yellow portion, - - - - -	—	0.32	
Brick from Cuestrinchen, pale red and dark yellow:			
Red portion, - - - - -	—	0.14	2.49
Yellow portion, - - - - -	—	0.15	0.11
Stove tiles from Stettin, dark red and light yellow:			
Red portion, - - - - -	4.90	0.29	14.71
Yellow portion, - - - - -	5.50	0.27	0.52

In most cases brick clays contain larger or smaller amounts of organic substance which is destroyed in heating, and in many cases can bring about a reduction of the ferric oxide. Thus Rathenow clay, slightly heated in a covered crucible, contained 2.20 per cent of ferrous oxide. The ferrous oxide formed seems very unstable on igniting in the presence of air and goes over into ferric oxide. The above-named sample of Rathenow clay contained only 0.76 per cent of the lower oxide after igniting one hour in air, and the small amount of ferrous oxide (0.1 to 0.3 per cent) observed in all cases with normally burned brick must be looked upon as a remnant that has escaped oxidation. Clay wares containing much ferrous oxide produced by blue smoking, have a bluish black to graphite-gray color, a color which can be produced by heating brick of any color whatever in a current of hydrogen gas. This dark color is, however, very unstable at higher temperatures. If air were able to enter the kiln through

cracks, while the cooling is going on, smoked brick take on their original color, and it is very difficult to preserve the gray or black color. From this and the above analytical proofs it is evident that the yellow color of a clay can in no case be explained by the amount of ferrous oxide in it, and therefore the red color of yellow bricks after or during the burning has nothing to do with the oxidation of the iron, since even in the yellow bricks the iron is present as ferric oxide. I have shown elsewhere<sup>1</sup> that a red color can appear in clays containing lime if the lime takes up sulphuric acid from the fire gas; and since the calcium sulphate formed is decomposed by the silicic acid only at a temperature lying above that of the burning temperature, the lime cannot act on the iron oxide which then remains as the sole coloring constituent. In the two last mentioned clay bodies that were colored yellow and red, the cause of the coloration is to be referred to this cause according to the determinations of sulphuric acid made.

There is a second cause for the red color of calcareous clays, and this holds true when the temperature of burning is not sufficiently high to render all of the lime completely active; I believe that Mr. Mendheim's observation is to be traced solely to this cause.

It is a well-known fact that very high temperatures as they are used in the production of iron and the manufacture of porcelain, are attained only if a surplus of combustible gases is present in the flame, or if we burn with an intense flame, as it is expressed. In a kiln in which the mixture of the gases is in part oxidizing and in part reducing, the temperature in all cases is lowest where an excess of air is present. The cause of the red coloration in the case mentioned is not to be ascribed to the oxidizing effect of the excess of air, but to the circumstance that through it the temperature was lowered. Even in case a formation of ferrous oxide has taken place by burning under the influence of reducing fire gases, the burned products, especially in a continuous kiln, are under the influence of a current of

<sup>1</sup> Notizblatt, 1872, No. 4.

strongly heated atmospheric air sufficiently long to allow a partial or complete change to ferric oxide to take place.

This is shown by the following experiment: A prism of Senftenberg clay, about 1 cm. thick and 8 cm. long, which by strong burning had taken on a buff color (ferric oxide, 3.28 per cent, ferrous oxide, 0.14 per cent), was broken into two parts and the one heated for some time in a current of hydrogen to a moderate red heat and allowed to cool in the current of the gas. After breaking, the clay showed a uniform ashen gray color. A gray-colored piece was now heated about two hours in a crucible in the presence of air. After cooling, it was again colored yellow through and through and the shade corresponded entirely with the original one.

That not only in porous clay, as in this experiment, but also in vitrified clays like porcelain, a change to ferric oxide takes place during cooling (of course, somewhat retarded by the density of the mass) is shown by the examination of the clinker from Schwarzhuette. It had, externally, a very intense and pure red color and when broken showed itself completely vitrified and very homogeneous. In the middle of the brick there appeared a red core whose color agreed with the color of the surface surrounded by a darker zone about 2 mm. wide. The color gradation was the same on both sides and had the following shades from within towards the outside: Cherry-red, grayish red, grayish green, blackish violet, grayish green, grayish red, and cherry red; the external red color, the real color of the brick, appeared in a layer not exceeding 1 mm. at most places. The grayish red part likewise had only a slight extent and no material could be obtained for an analysis. The cherry-red, grayish green, and violet portions, however, were examined. The analysis showed:

	Cherry-red. Per cent.	Grayish green. Per cent.	Blackish violet portion Per cent.
Silicic acid, - - -	79.43		
Alumina - - - -	10.07		
Ferric oxide, - - -	5.35	3.43	2.14
Ferrous oxide, - - -	0.12	1.85	3.01
Lime, - - - -	trace		
Magnesia, - - - -	1.40		
Potash, - - - -	2.36		
Soda, - - - -	1.62		
	100.35		

The color, therefore, becomes darker with a larger amount of ferric oxide.

The phenomenon can be interpreted in no other way except that setting out from the surface a reduction of ferric oxide to ferrous oxide took place under the influence of the flame without transmitting the effect to the innermost part of the brick; later on, cooling and oxidation took place again, likewise beginning at the surface which has completely restored the normal color of the brick at the surface and in the lower part has produced at least a decrease in the amount of ferrous oxide without reaching those parts in the interior of the body that have been most reduced.

The determination of the ferrous oxide beside the ferric oxide, which formerly offered some difficulties with silicates not decomposed by acids, was carried out according to a modification of Finkner's method which has also been used by Prof. Remmelé in his contribution: "Remarks Concerning the Oxidation Conditions of the Iron in Clays and Some Reactions in Brick Kilns." In place of the potassium fluoride finely powdered naturally occurring cryolite (sodium and aluminum fluoride) free from iron was used. The method was carried out so that 1 gram of the extremely finely ground material, together with 2 grams cryolite, was treated in a large platinum dish with 25 cc. of dilute sulphuric acid and boiled for some time. The decompo-

sition of the silicate, the completion of which may be known when the liquid, at first dark-colored, has become entirely colorless and almost clear, rendered slightly turbid only by the precipitated silicic acid or calcium sulphate takes place after boiling from fifteen to twenty minutes. Then, after thorough cooling, the liquid was diluted with one-half liter of water and the quantity of the dissolved ferrous oxide determined in the usual way with a solution of potassium permanganate. The determination of the total content of iron was done in the ordinary way by reduction in a sulphuric acid solution by means of amalgamated zinc and platinum and titrating with potassium permanganate. From the total content of iron and the difference of the ferric oxide corresponding to the ferrous oxide, there is obtained the quantity of ferric oxide present. In order to exclude any errors which might be caused by impurities of the cryolite or sulphuric acid a blank determination was made by dissolving 2 grams of cryolite alone in 25 cc. of dilute sulphuric acid boiling, diluting with one-half liter of water and titrating with permanganate solution. The red color, indicating the absence of reducing substances, is shown immediately after adding the first drop.

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### The Influence of Fire Gases upon Clays and the Color Phenomena Connected with It

PROF. CHAS. W. MESLOH, TRANSLATOR

The color changes which differ from the ordinary ones peculiar to clay and which are caused by the burning process in the case of unglazed wares are due to two causes:

1. A more or less energetic chemical action which is produced by the increased temperature alone or by the effect of constituents contained in the fire gases.
2. A greater or less increase in the specific gravity of the mass by vitrification, a physical change.

By examining these causes more closely, and later on learning to know the burning process better, we are enabled to judge

to what causes the irregular coloration, especially prominent in the continuous kiln, is to be ascribed; not only upon the coloring phenomena appearing in the continuous kiln, but also upon those in other kilns will the following investigation shed more light.

In order to determine the chemical influences to which clay wares are subjected during the burning process it would seem necessary on account of the variety of the constituents occurring in the fire gases and the different behavior of clays towards them, as well as in regard to the complexity of the phenomena to adopt the synthetic way of producing the phenomena of coloration artificially and noticing the chemical changes of clays connected with these color phenomena.

In this way we are enabled to refer the individual color phenomena to the effect of a single or several substances acting at the same time, and in the course of our investigation we shall see that this way leads to very interesting results capable of direct application in the practical management of kilns, results which will explain nearly all the color phenomena occurring in practice and, therefore, may claim the greatest interest.

The constituents of fire gases whose effect on clays has been investigated, may be divided into normal constituents, that is, such which appear in every combustion no matter what kind of fuel is used, and which may be oxidizing or reducing, and accidental constituents which owe their presence in the fire gases to the impurities of the fuel used.

As normal constituents of the flame we may consider, nitrogen, oxygen, carbon dioxide, carbon monoxide, hydrogen, ammonia, hydrocarbons, and water vapor, and as accidental constituents present in nearly all fire gases, sulphur vapor, hydrogen sulphide, carbon disulphide, and sulphurous acid. As indifferent substances, even at a high temperature, there are left out of consideration, nitrogen and carbon dioxide and also water vapor, because it has injurious effects only at a low temperature at which its condensation and absorption by the pores of the unburned clays takes place.

These substances were produced in the purest condition possible. This is not the place to enter into a discussion in regard to their production ; I will only indicate what clays were investigated and in what manner they were acted upon.

In the previous chapter I divided the clays into four classes in regard to color phenomena that appear on burning, and subjected one representative of each kind to an examination as appears from the following:

1. Clays burning yellow, containing iron and lime—clay marls. Representative : brick clay from Birkenwerder.
2. Clays burning red, containing iron, low in alumina, free from lime—the red burning brick clays and loams. Representative : clay from Rathenow.
3. Clays burning white or yellow, free from lime, low in iron—pipe clays, plastic fire clays, lignite clays. Representative : clay from Greppin, near Bitterfeld.
4. Clays burning white, low in iron and high in alumina—kaolins. Representative : kaolin from Zettlitz.

Of these four clays, small rectangular tiles about 4 to 5 mm. thick were made and several of them placed together into a large platinum crucible covered with a porcelain lid provided with a hole ; thereupon the gas, whose effect was to be studied, was conducted into the crucible in a strong current by means of a fine porcelain tube so that the crucible could be heated to a bright red heat by means of three gas burners.

#### DIVISION I.—COLOR PHENOMENA OF THE YELLOW BURNING CLAYS CONTAINING LIME (BIRKENWERDER CLAY)

The effect of oxygen alone, introduced in a current of air into the crucible, showed the following colors after heating :

- At dark red heat—a dirty red ;
- At moderate red heat—flesh color ;
- At strong red heat—yellow with brownish cast.

The chemical change of clays connected with these colors, consists in the expulsion of the water and carbon dioxide, combustion of the organic substance, oxidation of iron compounds

to ferric oxide and union of the ferric oxide and lime with the silicates of the clay to a combination of a light color.

For practical work we can deduce the following conclusions :  
*"When there is a large amount of unused oxygen present in the fire gases the clays containing lime take on a color which varies according to the temperature, between dirty red and light yellowish brown."*

*Influence of hydrogen.*—The influence of pure hydrogen, even when it acted only for a short time, with the precaution that the cooling of the samples took place under exclusion of air, which was brought about by supplying the hydrogen until they were quite cool, showed an intense uniform blackening of the mass appearing on the surface as well as in the interior. This dark color, however, disappears after a short heating in the presence of air; that is, in the presence of oxygen. Those colors then reappear which are produced on heating in an atmosphere containing oxygen, only with the difference "*that the flesh color has a whitish cast at a moderate red heat, and the yellow has a yellowish green tinge at a bright red heat.*"

This darkening cannot come from carbon since it appears in test pieces, which had been previously heated, and with the use of pure hydrogen, but has its cause in the reduction of the iron compound, first to ferroso-ferric oxide, then to the ferrous oxide, and finally to metallic iron (as will be shown later on). On heating in air this blackening vanishes again, and after two hours we find no ferrous oxide, but only ferric oxide present in the clay. Accordingly, also the light colors of calcareous clays are to be ascribed to an oxidizing effect of the air on burning or cooling.

Quite the same phenomena as hydrogen produces, are produced by the other reducing agents found in the fire gases, carbon monoxide, carburetted hydrogen, and ammonia.

Reducing agents, therefore, may be said to bring about a darkening which, on supplying air, changes again to the colors characteristic for burning in air. *After previous reduction, however, the colors brought out again by the effect of the oxy-*

*gen are lighter, passing into white or light green, then without such a previous reduction.*

*A temporarily reducing flame in the kiln, therefore, contributes very much to developing the light color of clays containing lime.*

Of especial interest were the phenomena which are produced by the sulphur compounds in the fire gases, since I have stated before that the intensely red flashes and spots which form during the burning—especially in the continuous kiln—owe their origin to a considerable amount of sulphuric acid that it has taken up.

A sample of Birkenwerder clay heated for two hours at a dark red heat in a mixture of sulphurous acid and air was colored dark reddish brown and contained 13.60 per cent of sulphuric acid.

The same clay heated in a current of illuminating gas, fed at the same time with carbon disulphide, smelled very much like hydrogen sulphide when breathed upon and contained 6.75 per cent sulphur. On heating in the air the leather-brown color vanished with the evolution of sulphuric acid and passed over into the same striking red-brown color which appeared by heating in sulphurous acid and air. After this reoxidation the content of sulphuric acid was 14.11 per cent.

Heating the clay in an atmosphere of sulphur vapors or hydrogen sulphide or in mixtures of hydrogen, carbon monoxide or illuminating gas with sulphurous acid, produced the same phenomena as with carbon disulphide.

Sulphur compounds of all kinds in the fire gases, whether in the presence of oxygen or absence of the same, and consequent presence of combustible gases, are taken up with great eagerness by the lime clays under the formation of calcium sulphate, calcium sulphide, and iron sulphide; in the presence of oxygen the latter two also cause the formation of calcium sulphate.

This reaction is accompanied by an intense red coloration of the clay, pronounced at the surface and weakening towards the interior. The clay, colored red by sulphur compounds taken up,

loses its color completely when kept for some time in a reducing atmosphere, free from sulphur, the sulphuric acid being decomposed by the reducing influences into volatile sulphurous acid and the lime is again taken up as silicate. This reaction, directly opposed to the previous one, takes place only at a high temperature and not at a moderate red heat.

In a test-piece which showed 14.11 per cent of sulphuric acid, this amount of acid was reduced to 2.31 per cent by heating half an hour in a current of illuminating gas and subsequently heating in the air when the dark red color of the sample had passed into yellowish green.

*"In the presence of oxygen as well as in the presence of reducing gases (carbon monoxide, hydrocarbons, hydrogen, etc.), sulphur compounds are absorbed in large amounts by the iron and lime of the clay marls at a slight or moderate red heat. This absorption is always characterized by a very intense red color of the clay."*

*The pronounced red brought about by the absorption of sulphuric acid is completely destroyed at a high temperature and changed to the normal greenish yellow color by the action of reducing gases (hydrocarbons, hydrogen, and carbon monoxide).*

#### DIVISION II.—COLOR PHENOMENA OF RED BURNING CLAYS CONTAINING IRON AND FREE FROM LIME (RATHENOW CLAY)

The phenomena which appear due to the influence of the fire gases upon this class of clays which are used frequently for the manufacture of brick and terra cotta, are not near so prominent as in the ones mentioned before, and they cause much less difficulty with reference to the production of pure colors. The various shades of color are here produced chiefly by the smaller or greater amount of coloring ferric oxide and the degree of density which the clays attain in burning.

The action of air alone during the heating caused the characteristic red color of the clay to appear, which is the deeper, the higher the temperature applied. The chemical change of the

clay consists in the expulsion of the chemically-bound water, the burning of the organic substances and the changing of all iron compounds to ferric oxide.

*Through the influence of hydrogen*, as well as of the other above-named constituents of fire gases which, like it, have a reducing effect (carbon monoxide, hydrocarbons, ammonia), identical phenomena appear, as we have found in the case of the Birkenwerder clay,—only with a more intense coloration on account of the greater amount of iron contained in the Rathenow clay. The trials of the Rathenow clay ignited in a reducing atmosphere, appeared grayish black with the use of pure hydrogen, when the time of action was short, but velvety black, with a longer time for the reaction. On account of the larger amount of iron, this clay offered a better opportunity for a more careful investigation of the effect of hydrogen. This can only extend to iron compounds since its combinations alone can be affected by reducing or oxidizing influences at the burning temperature.

Several small tiles of Rathenow clay, weighing altogether 10 grams, were strongly ignited for some hours in a current of air until repeated weighings indicated no loss of weight. An examination of a tile then taken out showed that all iron compounds had been changed to the red coloring ferric oxide. The amount of ferric oxide was 7.27 per cent. Now the samples were heated in an atmosphere of pure hydrogen. In this they suffered a loss of weight, because the ferric oxide contained in it was changed to a lower state of oxidation by the loss of oxygen. From this loss in weight we can find, by calculation, how far the effect of the hydrogen or of the other constituents of the gases acting in an analogous manner, has extended. This is not the place to discuss these calculations; it is sufficient to give the results.

After heating for two hours in an atmosphere of hydrogen, at a cherry-red heat, the Rathenow clay contained 1.97 per cent of ferric oxide and 4.77 per cent of ferrous oxide; after heating two hours more at a light red heat it contained 0.88 per cent

of ferric oxide and 5.53 per cent of ferrous oxide, and after a stronger heating for two hours 0.00 per cent of ferric oxide, 6.01 per cent of ferrous oxide, and 0.21 per cent metallic iron. In all cases the color was black, and the darker, the higher the temperature.

From this it follows, supported by the analogous behavior of calcareous clays, that the color which is produced in clay, by the ferrous oxide which is formed by reducing influences, is *black* and not *white*, as has been frequently assumed; and that moreover, with a long-continued action of these influences (perhaps more rapidly by carbon monoxide and hydrocarbons), the effect can go as far as the separation of metallic iron. The dark color produced by reducing influences in the case of clays containing much iron, is very unstable as we have seen from the preceding experiments, and the process is reversed with the admittance of oxygen at a red heat. After a short ignition, in the presence of air, the normal red color appears again, by the change of iron compounds into ferric oxide, but not with the same brightness which the clay had shown before.

*Reducing* influences which appear in a kiln at times are not favorable to the development of the most desired pure brick-red color, contrary to what was observed with the clays containing lime.

The influence of compounds containing sulphur likewise proved to be quite different from that noted in the case of clays containing lime which were discussed before.

Sulphurous acid in an oxidizing flame, whose effect was expressed in these experiments by heating the clay in a mixture of sulphurous acid and air, showed neither a chemical nor a color change.

Sulphur compounds in the presence of reducing gases are, on the other hand, absorbed by the clay with a formation of iron sulphide and simultaneous blackening. After a short heating in a current of illuminating gas fed with carbon disulphide, the Rathenow clay showed a sulphur content of 2.99 per cent.

On heating in the air this sulphur again burns out completely; the red color, too, returns with a violet tinge and brighter than before. Hydrogen sulphide or mixtures of sulphurous acid with hydrogen, carbon monoxide, or hydrocarbons, have the same effect as carbon disulphide. With clays containing much iron, but free from lime, the presence of sulphur compounds in the gases of the kiln has no effect when air is in excess. But in the presence of reducing influences they are favorable to the production of a bright red color.

DIVISION III.—COLOR PHENOMENA OF THE YELLOW BURNING  
CLAYS, LOW IN IRON AND FREE FROM LIME  
(Clay from Greppin, near Bitterfeld.)

These clays are characterized by assuming, when heated in the presence of air at a low temperature, a pale red or yellowish red color (flesh color), which passes over at a higher temperature into yellowish white and at the brightest red heat into sulphur-yellow or straw-yellow color.

Under the influence of reducing gases the color changes into black, as with other clays.

The Greppin clay was light ashen gray in color when heated to a dark red heat in the presence of pure hydrogen, and had an iron content of 1.69 per cent ferric oxide and 1.01 per cent ferrous oxide. After a longer heating at a bright red heat it was dark ashen gray with 1.81 per cent ferrous oxide and 0.34 per cent metallic iron.

From this it also appears that the presence of ferrous oxide produces a dark color which has nothing in common with the real clay colors.

This gray color also vanishes very rapidly in the presence of air; still the original shades do not again appear, but colors noticeably paler. The flesh color which marks the low temperatures has been changed to a whitish yellow, while with the higher temperatures a pure yellow appears.

A temporarily reducing atmosphere in the kiln must, there-

fore, as we note it in the first class of clays, also contribute to the development of the yellow color most desired with these clays.

Sulphur compounds have no chemical effect on clays of this kind in the presence of air, nor do they produce a change in color. On heating in a mixture of sulphurous acid and air, the clay absorbs no sulphur compounds and shows the same color as in air alone. Sulphur compounds in the presence of reducing gases are readily taken up by the clay mass, as was the case with the clays discussed before, and a gray color appears as we have always noted under the influence of reducing gases. After being heated for two hours in an atmosphere of illuminating gas and carbon disulphide, the Greppin clay gave a strong odor of hydrogen sulphide with a sulphur content of 2.77 per cent, and showed a dark ashen gray color. This sulphur burned out again completely, and with it disappeared the gray color on being heated in the air for a short time. The yellow color which characterizes the action of the air on these clays does not return, however, but a red color, strongest at the surface, penetrates the whole mass, which is the more intense, passing over into a violet-red, the higher the temperature, at which the action of the sulphurous reducing gases took place. This red color does not appear with like intensity under all circumstances; it is most intense with the action of carbon disulphide alone, or carbon monoxide containing carbon disulphide, less intense in the presence of hydrocarbons or hydrogen in a sulphurous atmosphere and cannot be produced by a mixture of hydrogen and hydrogen sulphide; also by means of sulphurous illuminating gas it is not always possible to produce the red color of the clay artificially. From this it appears that the presence of large amounts of hydrogen or hydrocarbons limits or prevents the formation of this peculiar red color, and that the presence of much carbon monoxide together with the sulphur compound assists its development.

By long heating in the presence of air this red color does

not disappear, not even at a high temperature. It does disappear, however, if the latter is not very high, by a repeated alternate action of reducing gases free from sulphur (illuminating gas, hydrogen, etc.), and air, in which case the ordinary yellow color of the clay again appears.

If the color was an intense red it no longer vanishes under the alternate influence of reducing and oxidizing agents, but passes through a brown-red into a leather-brown color.

The chemical process which accompanies these interesting color changes, so important for the industries, is not easily explained; with the red color no lasting chemical change of the clay has taken place, especially not an increase in the content of ferric oxide. If I attempt an explanation, however, it requires further experimental confirmation.

The iron in the clay is usually in a chemical combination with the other constituents, and in consequence produces only a weak yellow color, as is also the case with the clays containing lime. By a simple reduction of the ferric oxide to the ferrous oxide, the latter remains in this combination as it shows strongly basic properties and after the reoxidation nothing has been changed in the condition of this chemical compound. If this reduction is accompanied by an absorption of sulphur, iron sulphide is produced, which is not basic. The iron is taken out of its chemical union, and after its oxidation is changed into free coloring iron oxide which is only mechanically mixed with the clay mass. The effect of the sulphur compounds on the clays free from lime, may therefore be stated as follows: Sulphur compounds under oxidizing conditions exercise no effect on the clays; in a reducing flame they produce a red color throughout the whole mass, the production of which is assisted by the presence of gases high in carbon and diminished by hydrogen compounds in large quantities.

Oft-repeated alternate reactions of oxidizing and reducing gases in the presence of sulphur compounds, again cause this red color to disappear at a low temperature and with slight coloration, and at a high temperature change it to a buff-brown.

DIVISION IV.—COLOR PHENOMENA OF THE WHITE BURNING  
CLAYS, HIGH IN ALUMINA AND LOW IN IRON  
(Zettlitz Kaolin)

These clays, which are rarely or never used for the manufacture of brick and terra cotta, but are all important for the production of the finest wares of the clay industry, porcelain and white ware, behave essentially as the ones above mentioned. Under the influence of a higher temperature, in the presence of oxygen, they take on a more or less pure white color. This color is influenced more or less by the amount of iron in it, which is, however, always significant.

Under the influence of reducing gases they, like the other clays, experience a darkening of color which, however, does not exceed a light gray; this exists throughout the whole mass when hydrogen is present, on account of the small amount of iron, and shows a somewhat darker color only when the reducing gases contain carbon. Since these clays for the most part belong to the refractory clays, and in consequence of this show a considerable porosity on slight burning, the gray color produced by the action of the reducing gases vanishes very quickly and causes a pure white color again to appear (at least in the Zettlitz kaolin).

In presence of oxygen, sulphurous acid has no effect on these clays and is not able to produce any changes in color; on the other hand, as we have seen with the other clays, sulphur compounds cause remarkable color phenomena when reducing gases are present at the same time. Zettlitz kaolin heated for two hours, as in the previous experiments, in an atmosphere of carbon disulphide and illuminating gas, showed a sulphur content of 1.12 per cent. To be sure, this vanished again completely on heating in air. The color of the kaolin, however, does not become white again, but changes to a beautiful rose color. As in the previously discussed buff-burning lignite clays, this color, penetrating the whole mass, could be made the more intense the higher the content of carbon in the sulphurous reducing gases, and it was the weaker the more the hydrogen compounds pre-

dominated. By an alternate oxidizing and reducing condition of the fire gases, free from sulphur, it was made to vanish completely.

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### Studies in Regard to the Composition and Action of the Fire Gases in the Kilns of the Ceramic Industry

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PROF. CHAS. W. MESLOX, TRANSLATOR

Of all the processes comprised in the manufacture of clay wares, the burning process is without question the most important one, (1) because the economic success of the work depends largely upon the choice of the apparatus used for this purpose and the manner of conducting the burn, and (2) because no other process may exert upon the quality of the ware produced the same harmful or beneficial influence.

In burning clay wares, the first change brought about in the previously plastic and soft mass is that it can no longer be made into a paste by water, but retains the form given to it. This change is a chemical change, and is brought about by the expulsion at red heat of the chemically bound water of the clay. This chemical change of the clay mass at an increased temperature suffices only in the rarest cases to give to the products the properties required. The chemical changes must be accompanied by physical changes in order to convert the clay mass so easily destroyed into durable objects of use and art.

Of the physical changes the most important is that of vitrification ; that is, the melting of the individual constituents of the mass (not followed by a complete softening) and the consequent loss of the shape given to it artificially, but which only brings about a greater or smaller contraction, a closing of the pores, and gives a greater strength and a certain resistance to mechanical and chemical influences to the clay mass, by impreg-

nating, as it were, the non-fusible parts with a molten vitreous mass which subsequently hardens. Besides the increased resistance given by vitrification, a coating of a colorless or colored layer of glass is given to many clay wares (that is a glaze) in order to make them completely impervious to liquids, to decorate them, or to produce a more suitable base for other decorations than the porous clay with a dull surface.

The physical change of vitrification of the mass and melting of the glaze, always requires a higher temperature than is necessary to deprive the clay of its property of softening; in some branches of the industry, for instance, the manufacture of hard porcelain, it requires the use of the highest temperatures which modern technology can obtain in large kilns.

With the expulsion of the water from the clay the chemical action is not complete, but is rather just beginning by acting on those constituents constantly existing as impurities, or intentionally added to the mass or the glaze layer to give to them certain properties (color, luster, hardness, transparency, opacity, etc.). By the loss of chemically bound water the increased porosity of the clay allows greater action of external influences.

The changes in the body and glaze that appear at these temperatures are not confined to the non-volatile parts taking up a different molecular position in regard to each other and creating new compounds by mutual exchange of their constituents, but the compounds formed are subjected also to influences of the gaseous bodies which constitute the fire gases and thereby undergo new changes.

According to the present state of technology, heating to the required temperatures is only possible by the combustion of carbonaceous substances in the presence of atmospheric air. Besides carbon, the fuels contain hydrogen, oxygen, nitrogen, and frequently sulphur, and some incombustible mineral constituents which remain behind in the ashes. The air contains oxygen and nitrogen. In the combustion of carbon compounds there arise as final products, besides the completely indifferent and

therefore unchanged nitrogen, at a sufficiently high temperature and in the presence of excess of air, carbon dioxide and water vapor; with an insufficient supply of air there are formed besides these, carbon monoxide, hydrocarbons and solid carbon separated in the form of soot and carried away in the current of air. Besides these the fire gases may contain constituents coming from the ashes, volatile chlorine compounds, alkaline vapors, particles of ashes carried along in the form of dust, etc. The wares placed in the kiln for burning can in no case be protected from contact with these substances, but must necessarily remain in contact with them during the entire burn, since the whole kiln is filled with them. At most, a rapid change in the composition of the fire gases, which arises usually through very sudden changes in the supply of the air and fuel, can be moderated and the solid substances (ash particles and soot) kept off by enclosing the ware in saggers.

Of the substances formed in the process of combustion, nitrogen, carbon dioxide and water vapor are those which are least apt to cause changes in the composition of the clay and we may call them the indifferent constituents, although the complete indifference of the last two has not been fully proved, especially for very high temperatures. On the other hand, the other constituents, oxygen; carbon monoxide, hydrocarbons, and hydrogen, even at low temperatures, exercise a very great effect on the majority of substances which accompany the pure clay substance in the industrial products.

Only in extremely rare cases, and in a measure accidentally, will it happen that the reaction of air and fuel is so well balanced as to produce only those constituents termed indifferent (nitrogen, carbon dioxide, and water vapor). As a rule the conditions will be such that either oxygen predominates in the fire gases, or that, beside carbon dioxide, there appear carbon monoxide, hydrocarbons, and hydrogen, or that, as we can see from determinations given later on, oxygen is also present beside the gaseous constituents just mentioned. We can, therefore, never

speak of a flame as having no effect at all on the ware in the kiln throughout a burn, but at most only for moments. In general its constituents will react with the constituents of the clay of the bodies, glazes, etc., according to the principles of chemistry, and the reaction will be the deeper the higher the temperature, the greater the amount of material entering into action and the more the condition of the surface and the porosity of the clay mass permits the penetration of the gaseous constituents of the fire gases into the interior.

The action of the free oxygen on the one hand, and of the carbon monoxide, the hydrocarbons, and the hydrogen on the other hand, the last three possessing an analogous behavior and differing only in degree, is a very different one upon substances other than the silicate of alumina and earthy, non-reducible oxides, which are largely used for glazes and colors. Often the action of these two opposite effects is mutually neutralizing. Under the action of oxygen, carbonaceous substances are burned, the compounds of iron, manganese, copper, etc., pass over into oxides as high in oxygen as they can exist at the given temperature, and metallic sulphides are changed into sulphates with or without the development of sulphurous acid.

We call this effect oxidizing because it causes the formation of oxides. Under the influence of the other substances mentioned above, a deposition of the carbon in the pores may take place, the oxides of the metals lose a part or all of their oxygen according to the duration and intensity of the action, and are changed into oxides lower in oxygen (as in the case of the oxides of iron, manganese, copper, etc.), or the reduction can go to the separation or volatilization of the metals themselves (as with lead, zinc, tin, and others), while sulphates are in part decomposed with evolution of sulphurous acid and in part may be changed to sulphides of the metals. This effect, because by it the oxides high in oxygen are destroyed, is called deoxidizing or reducing. These are only a few examples of the reactions which may take place.

With a change in the composition of the gases there will likewise be a constant change in the action which will extend not only to the surface, but also more or less deep into the interior as long as the clay mass is porous and the glaze unmelted. With the closing of the pores by vitrification of the clay or melting of the glaze the action of the flame on the interior of the ware ceases on account of the lack of contact between the reagents, or is at any rate much retarded and weakened, confining the effect chiefly to the outer surface. Hence the process is stopped just at the moment when the closing of the pores took place.

In what way the changes taking place under the influence of a chemical reaction of the fire gases make themselves known externally, in how far they give to the burnt products the normal and intended properties, or how far they cause the numerous and unwelcome phenomena which are generally termed burning defects,—concerning all this we have but rare cases of positive explanations based on scientific information. For most cases a solution is still to be found and the views held by different technologists concerning cause and effect and the means of avoiding or producing them artificially, differ very much.

It, therefore, seems a problem well worthy of study, and interesting to all branches of the clay industry, to investigate the phenomena accompanying the burning process, to find those conditions under which the desired result may be attained with certainty, and, on the other hand, to make known injurious effects. On account of the complications of the many circumstances coming into consideration and the difference with which the same influences act on the same kind of material at hand, it is very difficult, and perhaps impossible, to gain any clear conception with the means of analytical chemistry alone; greater success is promised by the method of synthetic investigation, the production of the phenomena in question under known conditions, so that comparisons may be made.

However, in order not to extend such synthetic investiga-

tions, which have been carried out successfully for a series of phenomena within the field of the brick industry, to a scope beyond the measure of practical necessity, it appeared necessary, first of all, to determine the limits between which fluctuate the influences coming into consideration in the working methods developed by experience. An investigation, as extensive as possible, of the course of the combustion process with different kiln systems, in the different phases of the burn and in different zones of the kilns, appears important not only as a foundation entirely indispensable for further investigations, but also is of value for the practice inasmuch as it permits the manufacturer to see clearly with what means he and others are working, and with what success changes may be made in the use of his appliances. If such an investigation is to have not only a scientific interest, but also some practical value, it must be carried out on a larger scale and extended to as many objects of investigation as possible. In the last few years investigations concerning the composition of the fire gases have been published, but they extended only to a single system,—to the continuous brick kiln;<sup>1</sup> with other kiln systems and in other branches of ceramics, the views concerning the processes taking place rest more on suppositions than on definite knowledge.

The investigations communicated below pertain to the following kilns:

#### A. UP-DRAFT KILNS

1. Ordinary arched brick kiln of Mr. Radzijewski in Heegermuehle.
2. Two-story kiln, for white ware, of F. S. Oest Ww. & Co. in Berlin.
3. Two-story porcelain kiln of the Royal Porcelain Factory, in Berlin.

#### B. HORIZONTAL KILNS

4. Continuous brick kiln of a plant in Heegermuehle.

<sup>1</sup> "Investigations of the Composition of Fire Gases in a Continuous Lime Kiln." Notizblatt, of the German Society for the Manufacture of Brick, :875, No. 4.

W. Olschewsky: Deutsche Toepfer and Ziegler Zeitung, 1877, No. 53.

F. Fischer: "On the Examination of Fire Gases," Dingler's Journal, 1878, p. 171.

5. A partially continuous brick kiln of the Splau Clay Works, near Wittenberg.
6. Stoneware kiln of Mr. Joseph Schult, in Hoehr.
7. Stoneware kiln for mineral water jugs of Mr. W. Zoeller, in Grenzhausen.
8. Kiln for the burning of faience tiles of G. Schoeffel & Son, in Berlin.

#### C. DOWN-DRAFT KILNS

9. Kiln for the burning of stoneware pipes, of Mr. Simon Peter Gerz, in Hoehr.
10. Kiln for the burning of terra cotta ware, of E. March's Sons, in Charlottenburg.
11. Porcelain kiln of the Berlin Porcelain Company.
12. Continuous gas kiln of the Royal Porcelain Factory, in Berlin.

In carrying out the examination of the fire gases, the chief object was to produce as clear a picture as possible of the course of one or more burns, and to bring out the fluctuations differing most widely, according to the phases of the burn, at different places of the kiln. For this purpose the number of single determinations must be a very large one, and with some burns the number of samples taken and analyzed is more than eighty and the total number of analyses many hundred.

Although the large columns of figures thus produced may seem uninteresting, yet it is not desirable to summarize and simplify them in publishing the results of the investigation. The value of numerical representation does not always appear at the first glance, and much close study is required in order to draw all conclusions from them from different points of view. For this reason they often receive a new value when new points of view are added and new investigations either supplement or contradict them.

With such an extended investigation as the one under discussion, it was, of course, necessary, in order not to extend it over years, to find an analytical method which permits of as rapid execution as possible without lessening the desired accuracy. In this work there was used the method described in the

article, "On the Investigation of Industrial Gases." For the chemist there is only to be added the method of calculating the numerical values found. The method described in the article mentioned permits of the determination of carbon dioxide, oxygen and carbon monoxide by absorption and direct reading with more than the accuracy practically required. The quantity of the remaining combustible gases can be determined only by exploding the residual gas, after addition of oxygen and electrolytic gas, and subsequently determining the carbon dioxide produced in the explosion. There remains still to be determined, to what definable hydrocarbon products belongs the carbon contained in the gases. By a second explosion with addition of hydrogen and electrolytic gas, we can determine the quantity of oxygen remaining unused after the explosion. But then the method would have been taken from its proper place, as a rapid method to be used in a works laboratory as a means of controlling the burning. Such an extension, necessary perhaps for other scientific purposes, did not seem to be demanded by practice. The products of dry distillation (and the products of incomplete combustion are to be considered as such) are carbon monoxide, hydrogen, marsh gas, ethylene, and other hydrogen compounds still higher in carbon. The first three form the main constituents of illuminating gas, the ethylene being represented in it only by a few per cent, and the hydrocarbons still higher in carbon, benzene, naphthalene, etc., by very small quantities. Assuming the analogous behavior and the constant quantitative predominance of the hydrogen and light hydrocarbon (marsh gas,  $\text{CH}_4$ ) over the so-called heavy hydrocarbons, higher in carbon, the results of the one explosion carried out were so calculated that when the carbon content of the hydrocarbon compounds plus hydrogen was found to be less than that corresponding to marsh gas, the combinations were considered as a mixture of marsh gas and hydrogen, with a higher content of carbon as marsh gas and ethylene ( $\text{C}_2\text{H}_4$ ). For the present practical requirement, though not strictly correct from the scientific

standpoint, this method of calculation appears sufficient for the simplification necessary in a technically useful method.

In order to render the results of the examination clearer to the layman, it seemed necessary to condense them at least inso-much that the effect of the gases be expressed by one numerical value. A gas will possess a more intense oxidizing effect, the higher it is in the active agent, oxygen; it is the more reducing, the more ingredients it contains which consume oxygen in burning. Of such substances there are four given in the following tables: Carbon monoxide, heavy hydrocarbons, marsh gas, and hydrogen. But in order to obtain a numerical value for the reducing power of a gas it would not be correct to sum up the active ingredients in per cent by volume, as obtained from the analysis. The effect of the ingredients mentioned above in the fire gases depends upon their activity in drawing oxygen from the constituents of the clay or the glaze. The quantity of oxygen which they require for combustion, however, differs considerably, and hence the effect is proportional to the oxygen-consuming power, as is shown by the following statements:

1 part, by volume, of carbon monoxide, CO, requires  $\frac{1}{2}$  part, by volume, of oxygen and furnishes 1 part, by volume, of carbon dioxide.

1 part of heavy hydrocarbon, ethylene,  $C_2H_4$ , requires 3 parts of oxygen and furnishes 2 parts of carbon dioxide and 2 parts of steam.

1 part of marsh gas,  $CH_4$ , requires 2 parts of oxygen and produces 1 part of carbon dioxide and two parts of steam.

1 part of hydrogen requires  $\frac{1}{2}$  part of oxygen and furnishes 1 part of steam.

For this reason it is more convenient to take as a basis for the expression of the oxidizing or reducing power of the fire gases that quantity of oxygen which is present in excess, or which is lacking in order to produce perfect combustion. But since oxygen is never burned alone, but is always mixed with nitrogen in the proportion of 21 : 79 parts by volume, the quan-

tity of air has here been used as the basis and in the following tables a column is given<sup>1</sup> which expresses the ratio between the air actually taken to the fire, to the air theoretically required for combustion. The numbers higher than 100 indicate those gaseous mixtures which are oxidizing, and those lower than 100 the fire gases of a reducing character. If thus in the column "Per cent of air" there is found the number 180, this means, that in place of 100 units of volume of air, which were required in order to burn all the carbon and hydrogen compounds to carbon dioxide and water, 180 units of volume, that is 80 too many, were conducted to the fire. If the number is 80, in place of 100 units of volume, there were brought in only 80, that is not enough for complete combustion by 20.

#### A. UP-DRAFT KILNS

##### *1. Brick Kiln of Mr. Radziewski at Heegermuehle*

The kiln is an arched, so-called German kiln, about 10 meters long, 4 meters wide, and 4.5 meters high; on one of the two lateral sides it is provided with eight furnaces whose grates extend across the kiln and are charged with fuel from one side. Pine wood is used as fuel. In the arch there are 102 short chimneys arranged in five rows, each opening being 12 cm. in diameter, and, as usual, the flow of gas is regulated by covering with brick. The samples were taken through iron pipes, coated on the inside with a slushy mixture of finely ground sand and boracic acid for protection against oxidation, inserted in one of the doors of the front walls so that the pipes extended about 1

<sup>1</sup> If the quantity of nitrogen found by analysis is represented by N, the quantity of oxygen which the combustible gases still present would consume for complete combustion by O, then the quantity of nitrogen corresponding to this oxygen is  $\frac{79}{21}O = 3.76 \times O$ , and accordingly the quantity of nitrogen belonging to the air required for theoretical combustion =  $N + 3.76 \times O$ .

The air, however, actually introduced is to the quantity of air theoretically required, as the corresponding quantities of nitrogen, that is, as  $N : N + 3.76 + O$ , according to which the proportion is easily calculated. If the oxygen in the fire gases is in excess the  $+O$  becomes  $-O$ .

meter into the kiln. The pipes were of 1 cm. inside diameter. The one pipe was introduced about 0.1 meter below the arch, another 1.5 meter above the grate. The samples were taken on two succeeding days, on the first during the full heat, on the second during the so-called "finishing." The product is known on the Berlin market as Heegermuehle face brick, and is manufactured from a marl-like clay containing about 15 per cent of calcium carbonate and 6 per cent of iron oxide. The color of the brick, when well burned, is sulphur- to lemon-yellow; of the vitrified brick, yellowish green. In the upper part of the kiln there are always reddish and brownish flashed brick.

The time stated in the table, enabling one to estimate the time elapsing between the taking of samples, is referred to the beginning of sampling which, when not otherwise specified, took about five minutes.

The numbers following in the horizontal rows always refer to samples taken at the same time.

The results of the analyses are contained in Table I.

On comparing the columns of figures in the horizontal direction with each other and considering the numbers representing the per cent of air used as the total expression for the entire analysis, one observes that between the upper and lower numbers of the kiln there are no considerable differences in composition, until the fire burns down, when the quantity of excess air increases more rapidly in the lower part than in the upper. This is due to the arrangement of air admission and exit of the gases.

Besides, the analyses show two phenomena which do not agree with the most popular views concerning the course of the process of combustion. The first is that with the appearance of considerable amounts of unburned gases the oxygen need by no means vanish from the fire gases. There may be several causes for this which may in part work simultaneously; namely, first a change in the composition of the fire gases and a transition from the reducing condition to the oxidizing condition

TABLE I  
BRICK KILN OF MR. RADZIJEWSKI AT HEEGERMUEHLE

Aug. Day.	A.M. Hour.	Details and observations.	Sample : 0.1 m. under the arch. 1½ m. above the grates.															
			Per cent of air.	Nitrogen.	Oxygen.	Hydrogen.	Methane gas.	Heavy hydrocarbons.	Carbon monoxide.	Carbon dioxide.								
11	9.25	Immediately after firing, black smoke	16.5	0.2	0.0	0.0	3.0	80.3	116	14.2	0.6	0.0	0.2	0.0	3.9	81.1	117	
9.40	-	Some time after firing, smoke just disappeared	-	-	0.0	0.0	0.0	7.3	82.5	132	8.5	0.0	0.0	0.0	9.4	82.1	176	
10.05	-	Fire burnt down low, immediately before a fresh firing	-	10.2	0.0	0.0	0.0	-	-	-	-	-	-	-	-	-	-	
10.15	-	Immediately after firing, thick black smoke becoming gray by the end of taking of the test	-	3.1	0.0	0.0	0.0	16.1	80.8	398	2.7	0.0	0.0	0.0	17.0	80.3	490	
10.30	-	Smoke entirely disappeared	-	19.7	0.1	0.0	0.0	2.9	77.3	115	16.5	1.0	0.1	0.3	0.0	4.1	78.0	115
10.40	-	Fire burnt down, just before a fresh firing	-	8.4	0.0	0.0	0.0	9.1	82.5	170	9.5	0.0	0.0	0.0	8.5	82.0	164	
12	8.50	At the conclusion of the burning of the kiln, $\frac{1}{3}$ of the exit holes covered, immediately after a very heavy firing, thick black smoke, smell of sulphurous acid	-	3.9	0.0	0.0	0.0	14.7	81.2	322	3.3	0.0	0.0	0.0	15.7	81.0	369	

TABLE I—Continued.

Day.	Hour.	Details and observations.	Sample : 0.1 m. under the arch. 1/4 m. above the grates.										
			Per cent of air.	Oxygen.	Nitrogen.	Hydrogen.	Methane gas.	Heavy hydrocarbons.	Carbon monoxide.				
Aug. 12	9.20	Fireplace completely filled, thick black smoke, smelling of sulphurous acid - - -	-	-	24.3	2.1	0.0	0.7	1.2	0.3	71.4	86	
12	9.50	Smoke almost disappeared - - -	16.8	0.2	0.0	0.0	0.8	82.2	104	13.0	0.0	0.0	106
12	10.15	Fireplace completely filled, very thick black smoke, smelling of sulphurous acid - - -	-	-	-	-	-	-	25.8	0.4	0.0	0.0	102
12	10.45	First fireplace by the test-hole walled up, the others fired - - -	18.8	0.2	0.0	0.0	3.3	77.7	118	6.7	0.0	0.0	14.2
12	11.30	Four fireplaces by the test-hole walled up, the others fired gray smoke at the end of kiln, where the test is taken - - -	20.4	0.0	0.0	0.0	0.9	78.7	185	1.2	0.0	0.0	19.1
12	12.30	After conclusion of the burn and daubing of the kiln - - -	4.5	0.0	0.0	0.0	12.4	83.1	228	1.6	0.0	0.0	18.2
												80.2	686

\* The glass flask which served for the preservation of the samples of gas was broken in the journey.

during the duration of the experiment; second, an insufficient mixing of the air in the kiln; third, slow action of the oxygen on account of the great dilution with indifferent gases and too low a temperature.

The second phenomenon is that an appearance of heavy black smoke is no sure sign that unburnt gases appear in noteworthy amounts in the kiln; on the appearance of smoke the flame has frequently still an oxidizing character. The reducing gases (carbon monoxide, hydrocarbons, hydrogen) are completely colorless, and in outward appearance cannot be distinguished from atmospheric air. The color is given to the smoke, not by these, but by tar vapors at a low temperature or by carbon in extremely fine particles, at a higher temperature, produced by the decomposition of tar vapors which are formed at the beginning of the heating of the fuel, and after a time collect into flakes of soot. Whether or not this solid, separated carbon is consumed completely on passing through the red hot part of the kiln depends upon the amount of oxygen available for combustion, or on its dilution by indifferent substances and on the temperature. The combustion of the carbon will be all the more slow and require all the more time the lower in oxygen the gases are and the lower the temperature. At any rate, the solid carbon is not consumed as readily as the gaseous carbon compounds on account of the greater density and the slight mobility of the particles, and if we see the carbon compounds appearing in the flame at the same time with free oxygen, the solid carbon may be expected with even a greater content of oxygen. In fact the smoke does not wholly disappear until the fuel has been thoroughly heated and the free oxygen has increased considerably.

In former communications<sup>1</sup> the causes have been set forth, why in burning marl clays a temporary maintenance of a reducing flame in the kiln is necessary to develop in its purity the

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<sup>1</sup> Thonindustrie Zeitung, 1877, No. 3, et seq., "The Importance of the Continuous Kiln for the Clay Industry."

yellow color peculiar to these clays. This is necessary in order to decompose the calcium sulphate, which is formed on the surface by the action of oxygen and sulphurous acid coming from the sulphur of the fuel or the clay, since otherwise the iron oxide of the clay would be kept from vitrification. The reducing atmosphere necessary cannot be obtained with certainty with the usual manner of firing, as is proved by the samples taken on the first day of the experiment, but it appeared only when the outflow of the flame was obstructed and the supply of the fuel was increased as much as the size of the flues would permit. In fact, the smoke leaving the kiln on the first day did not show the least odor of sulphurous acid, while in the last phase of the burning, which the brick-maker calls the "burning out," and in which he fires heavily with a weakened draft, the smoke possessed a suffocating odor of sulphur after every charge of fuel; when the smoke ceased the sulphur odor also vanished. During the closing of the kiln there appears a partially oxidizing, and after the complete closing an intensely oxidizing, atmosphere throughout the kiln so that through the first cooling there may be assumed an equalization of temperature but not a chemical reaction which could contribute to the further development of the yellow color of the clay.

The phenomenon that the upper part of the kiln always contains red spotted brick finds its explanation, partly in the lower temperature at which the sulphur compounds which the clay has taken up are decomposed more slowly, and partly, in the fact that the reducing effect of the gases in the upper parts becomes weaker, since a part of the gaseous carbon and the hydrogen compounds is consumed in the lower part of the kiln by means of the oxygen of the ferric oxide contained in the clay and the decomposition of the sulphates.

2. *Two-Story White-Ware Kiln of F. S. Oest Ww. & Co., in Berlin.*

The kiln is a circular old-fashioned white-ware kiln with two stories, each about 3 meters in diameter and 3 meters high.

Each of these spaces has four fireplaces arranged for coal, with iron grates and ash pans filled with water. The area of each grate is about one-third of a square meter. The openings for charging the fuel are in the top of fire-boxes built in front of the kiln and are covered with a fire-clay tile after firing.

The flame enters the kiln space above the bottom of the kiln, through an opening 25 cm. square, and is distributed without flues between the piles of saggers. The arch of the lower kiln is pierced by a number of passageways which allow the flame to enter the upper kiln. The latter contracts to a chimney which is about 12 meters high. The lower kiln was filled with fine faience ware, enclosed in fire-clay saggers for the biscuit burn, without any glaze; the upper kiln was filled with fire-brick.

The firing of the kiln took place at intervals of one to one and one-fourth hours, all four fireplaces being charged successively. Before putting in the fresh coal the coke on the grate was shoved to the rear and then a larger amount of lump coal, about  $\frac{1}{2}$  hektoliter for each fireplace, was put in. The burning of the faience ware in the lower kiln lasted from five o'clock in the evening until half-past one the next afternoon, that is, twenty and one-half hours. The burning in the upper kiln lasted until seven o'clock in the evening, that is, five and one-half hours.

For the taking of samples two porcelain tubes 15 mm. in diameter were so inserted into the door openings of the upper and lower kiln that the one was on the right and the other on the left side of the door. The tubes extended about 1 meter into the interior of the kiln and took the gases from the lower kiln 0.5 meter under the arch and 0.5 meter above the floor, in the upper kiln 0.3 meter under the arch and 0.3 meter above the floor.

Three samples were always drawn at the same time from the kiln; during the burning of the lower kiln two were taken from it and one from the upper kiln through the tube 0.3 meter

under the arch. During the burning of the upper kiln two samples were taken from it and one from the lower kiln already closed and cooling, through the tube 0.5 meter under the arch.

The results of the investigation are shown by the tables II $a$  and II $b$ . As may be seen from the tables the process of combustion takes place in a quite different manner from that of the preceding kiln.

If we compare first the amounts of air which are supplied to the fire in the lower and upper kilns we see that they are always larger in the upper than in the lower; this is explained by the fact that the already very old and cracked kiln allowed much air to pass through its walls and the upper fireplaces were only superficially daubed with clay which did not completely stop the supply of air. In the period of the greatest evolution of gas in the fireplaces, that is, from ten to twenty minutes after the supply of the fuel, there is in the lower kiln such a large excess of combustible gases that the air entering through the lower fireplaces is able to burn only a half or a third, and after a further addition of air through the crevices in the kiln the excess is still so large that about one-fifth of the products of combustion of the fuel passes out of the chimney unburnt. Not until the fire burns down does the amount of air in the kiln increase so far that it just reaches or slightly exceeds the amount theoretically necessary.

It is a surprising phenomenon that in the lower kiln, beside the large amounts of combustible gases both in the neighborhood of the floor as well as under the arch, there are always present considerable amounts of free oxygen; it is also surprising that the combustion is a very incomplete one and the mixture not intimate, while in the upper kiln, after the flame has passed through the openings of the arch this phenomenon disappears and the free oxygen, as far as it appears beside the combustible gases, is reduced to very small amounts.

An observation of the fire easily explains this. Immediately after the supply of considerable amounts of fuel the walls

**TABLE**  
WHITE WARE KILN OF F. S. OEST Ww. & Co.

Day.	Hour.	Details and observations.	Lower kiln.							
			Samples : 0.5 m. under the arch.							
			Carbon dioxide.	Carbon monoxide.	Heavy hydrocarbons	Meth. gas.	Hydrogen.	Oxygen.	Nitrogen.	Per cent of air.
July 26	P.M. 7.00 8.00 9.00 10.00	2 hours after lighting heating up	13.6 13.3 8.7 10.4	2.4 0.2 0.1 0.1	0.0 0.0 0.0 0.0	0.6 0.0 0.0 0.0	0.4 0.0 0.0 0.0	2.6 6.3 11.4 8.0	80.4 80.2 79.8 81.5	100 141 214 158
27	A.M. 5.50 6.10 7.10 7.40 9.00 9.15 10.00 10.50 P.M. 1.00	Fire burnt down, chimney free from smoke 10 minutes before firing Immediately after firing, thick black smoke Smoke almost completely disappeared, 20 minutes before firing Ten minutes after firing, thick black smoke Fire entirely burnt down, chimney free from smoke Ten minutes after firing, thick black smoke Chimney free from smoke, 30 minutes before firing Twenty minutes after firing, very black smoke Chimney free from smoke, 1 hour after firing. The end of the burn of the lower kiln	11.5 7.8 11.0 10.8 10.8 7.8 10.4 10.4 4.6	5.5 6.4 11.7 11.7 11.7 12.0 6.2 0.4 10.4	0.0 0.0 0.0 0.0 0.0 0.0 0.4 0.8 0.0	0.4 1.2 2.0 2.4 2.3 0.0 0.8 0.8 0.8	0.8 0.6 2.1 4.8 4.0 	4.1 7.6 0.7 2.5 2.5 71.4 78.2 75.5 79.6	77.7 76.4 72.5 71.1 71.4 65 92 106 97	101 109 66 63 65 50 92 106 97

**TABLE**

Day.	Hour.		Upper kiln.							
			0.3 m. under the arch.							
July 27	P.M. 2.00 3.30 4.30 5.00 5.45 6.10	Fire burnt down clear Immediately before a new firing Immediately after the firing, dark smoke No smoke at chimney Immediately before firing Last fire in burning off the kiln	11.0 13.3 16.4 14.7	0.0 0.6 0.2 3.0	0.0 0.0 0.0 0.3	0.0 0.0 0.0 0.0	0.0 0.0 0.0 0.0	7.3 4.9 0.8 0.0	81.7 81.2 82.6 82.0	150 127 103 90

## IIa

## BURN OF THE 26th AND 27th OF JUNE

									Upper kiln.						
0.5 m. above the floor of the kiln.									0.3 m. under the arch.						
Carbon dioxide.	Carbon monoxide.	Heavy hydrocarbons	Marsh gas.	Hydrogen.	Oxygen.	Nitrogen.	Per cent of air.	Carbon dioxide.	Carbon monoxide.	Heavy hydrocarbons	Marsh gas.	Hydrogen.	Oxygen.	Nitrogen.	Per cent of air.
12.2	2.0	0.0	0.5	0.0	4.4	80.9	112	12.1	0.4	0.0	0.0	0.0	7.1	80.4	148
12.0	2.8	0.0	0.0	0.0	5.8	79.4	127	6.5	0.0	0.0	0.0	0.0	13.4	80.1	201
6.8	0.2	0.0	0.0	0.0	13.2	79.8	161								
8.0	0.3	0.0	0.0	0.0	10.8	80.9	197								
13.8	2.6	0.0	0.4	0.6	2.0	80.6	97	15.7	0.0	0.0	0.0	0.0	2.1	82.2	111
12.4	6.5	0.0	1.4	3.0	0.4	76.3	74	17.4	1.8	0.0	0.0	0.0	0.1	80.7	96
10.4	11.2	0.0	2.0	2.3	0.2	73.9	65	14.3	4.1	0.0	0.8	0.8	0.2	79.8	83
9.0	14.6	0.0	2.3	8.6	0.0	65.5	52	14.0	0.0	0.0	0.0	0.0	5.5	80.5	135
10.2	8.5	0.0	1.9	3.5	1.3	74.6	70	13.2	5.7	0.0	1.0	2.0	0.1	78.0	78
11.5	3.7	0.2	0.4	0.0	5.4	78.8	111	14.4	0.8	0.0	0.0	0.0	3.1	81.7	114
5.7	11.3	0.0	2.7	2.7	5.1	72.5	73	12.9	3.7	0.0	0.8	0.8	1.7	80.1	86
12.3	5.1	0.4	0.0	0.0	3.3	78.9	97	15.8	0.0	0.0	0.0	0.0	2.3	81.9	112

## IIb

									Lower kiln.						
0.3 m. above the kiln floor.									0.5 m. under the arch.						
5.1	0.0	0.0	0.0	0.0	13.9	81.0	282	5.5	0.0	0.0	0.0	0.0	14.3	80.2	303
16.0	0.3	0.0	0.0	0.0	1.8	81.9	108	3.3	0.0	0.0	0.0	0.0	16.8	79.9	479
16.3	0.1	0.0	0.0	0.0	0.7	82.9	103	2.8	0.0	0.0	0.0	0.0	17.3	79.9	536
10.9	0.1	0.0	0.0	0.0	7.8	81.2	155	3.5	0.0	0.0	0.0	0.0	16.6	79.9	457
								2.3	0.0	0.0	0.0	0.0	18.3	79.4	1167

of the fire-box were so much cooled by it that the gases developed did not at once ignite, but passed unconsumed into the kiln, or alternately ignited and then went out again. The ignition could, therefore, only occur in the interior of the kiln, and since the movement of the gases is much slower there than in the fire-hole, on account of the greater area of the cross-section, the mixture of air and coal gas could only be incomplete. Not until the flame had passed through the small openings in the arch to enter into the upper kiln could the mixture become more perfect, and the combustion take place as far as the oxygen present permitted it. The burning of the faience ware, therefore, took place for the most part under a very intensely reducing kiln condition, excepting at the beginning, where the charges of coal were small for the purposes of slow heating. During the cooling, however, oxygen was present in great excess. If from the results of the analysis obtained from the main burn in the lower kiln we take the average of those samples which were taken during the slow fire, then of those taken immediately after charging, and finally of those with the fire burnt down in the lower kiln we obtain the following expressions for the supply of air, the theoretically necessary amount being put at 100, as in the large table.

	Slow fire. Per cent.	Immediately after firing. Per cent.	Fire burnt down. Per cent.
Lower kiln, under the arch -	153	86	89
Lower kiln, above the kiln floor	149	67	92
Upper kiln - - -	174	82	114

After the conclusion of the burn in the lower kiln, samples were still drawn from it in order to see whether gases did not move down from the upper kiln through the open passageways; but in general this need not be feared as the daubing of the lower fireplaces can never make them absolutely air-tight; air also enters the kiln through crevices, and this must always move upward.

*3. Vertical Two-Story Porcelain Kiln of the Royal Porcelain Factory*

The kiln used in the Royal Porcelain Factory for making experiments on a large scale, and for burning porcelain decorated under the glaze, is circular and has in the lower part a diameter of 1.5 meters and a height of 2 meters at the center of the arch. The biscuit kiln constructed above it has the same diameter and a height of 1.6 meters, and is connected with the glost kiln by a round central flue, 23 cm. in diameter and three square lateral flues with sides of 10 cm. The firing is done only with split pine wood in three slant grate furnaces; the fire-boxes have a length of 55 cm. and a width of 44 cm., but can be narrowed, according to requirements by fire-clay tiles inserted perpendicularly. The three fire-boxes open above have, at a depth of 45 cm., a projection in the wall 5 cm. wide which serves as a support for the billets of wood which are cut to the same length. Under this projection in the wall there is a pit 65 cm. deep, which receives the charcoal falling down from the hearth, and to which air is supplied for complete combustion by an opening at the side, 15 cm. wide and 8 cm. high. According to necessity the opening may be narrowed by the insertion of bricks. The air serving for combustion enters in part from above through the layer of wood, 45 cm. deep, in part through the openings in the lower box. The wood is always supplied as fast as it burns down so that the fire-boxes are constantly kept full. The flame passes through the flame holes into a ring-shaped flue, 20 cm. wide, in the bottom of the kiln above which a ring-like bench is formed by setting up fire-brick and covering them with tiles; on this bench the extreme ring of saggers is placed; the flame is forced through the spaces, 2 to 3 cm. wide, which have been left between the bricks of the bench into the kiln space proper. The burning lasts from fifteen to sixteen hours.

In all burns, in which the progress was investigated, the charge of the glost kiln consisted of porcelain, painted under the

glaze, with cobalt oxide colors and only in the lower parts, most exposed to the fire, of thick white porcelain.

The samples of gas were taken from the kiln partly through the door of the glost kiln by the insertion of porcelain tubes which extended 20 cm. beyond the first stand of saggers, partly in the biscuit kiln over the middle flue so that the tube ended in the flame coming from the same. On inserting the tubes into the glost kiln 0.5 meter above the floor and 0.5 meter under the arch, they were not placed perpendicularly over one another, but one on the right and the other on the left of the door. The samples were taken simultaneously, generally at intervals of an hour.

The tables III $a$ , III $b$ , III $c$  show the course of three burns.

The accompanying tables furnish a very instructive account of the course of the combustion in the porcelain kiln from a dark red heat to the conclusion of the burn, when the temperature reaches the melting-point of wrought iron,—the highest temperature which can be obtained in large kilns with the ordinary means of combustion. In consequence of the constant and uniform supply of fuel and the constant exit of the flames, only slight deviations appear in the composition of the gases in the various zones of the kiln as well as after successive intervals. Only from the time the fire-box is reduced, which causes a decrease of the fuel supply in the last stages of the burn, which experience has shown to be necessary, an increase of the oxygen content of the fire gas takes place or a lessening of the reducing effect of the kiln atmosphere as far as the oxygen is not present in excess. This change in the course of the firing coincides with the temperature at which body and glaze begin to soften and which causes the closing of the pores.

Among specialists the view is often held that it is absolutely necessary, for the burning of porcelain, to fill the kiln with a highly reducing gas, and that every access of free atmospheric air is to be avoided; if not, all kinds of defects, especially pock-

## COMPOSITION AND ACTION OF FIRE GASES

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TABLE IIIa  
VERTICAL PORCELAIN KILN. BURN OF THE 4TH OF MAY, 1878  
Samples taken in the flame of the middle fire in the biscuit kiln

Date	Hour	Details and observations.	Per cent of air.					
			Carbon dioxide	Carbon monoxide	Heavy hydrocarbons	Hydrogen	Oxygen	Nitrogen
May 4	A.M. 8.30	Fireplaces had been repaired before the burn.	12.9	0.8	0.0	0.3	0.0	5.7
	10.00	Beginning of the firing 3 o'clock in morning, dark red heat	17.2	0.0	0.0	0.0	0.0	80.3
	11.00	No red visible in biscuit kiln	-	17.9	0.2	0.0	0.0	80.7
	12.00	Beginning of white heat	-	18.0	0.5	0.0	0.0	80.1
	P.M. 1.00	Fireplaces reduced from 55 x 40 cm. to 55 x 32 cm. by introduction of fire-brick tiles	-	15.0	0.0	0.0	0.0	80.4
	2.00	Full white heat	-	15.0	0.0	0.0	0.0	80.8
	3.00	Full white heat	-	15.4	0.0	0.0	0.0	80.7
	4.00	Full white heat	-	15.0	0.0	0.0	0.0	80.4
	5.45	Full white heat	-	17.5	0.0	0.0	0.0	80.1
	6.00	Full white heat	-	15.3	0.0	0.0	0.0	80.6
	6.45	Last filling of the fireplaces. The end of the burn	-	15.8	0.0	0.0	0.0	81.5

N. B.—The fireplaces were not walled up.

The trial pieces drawn at 4, 5, and 6 o'clock had a feeble yellow color, but the porcelain in the kiln was pure white, and the blue decoration was deep blue and perfectly smooth.

TABLE III  
VERTICAL PORCHLAIN KILN. BURN ON THE 11TH OF MAY

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Porcelain was bluish white, the decoration with cobalt was less pure blue, and in many cases, especially in the thick spots and on the edges of the wares, was bubbled up and sunk in.

## COMPOSITION AND ACTION OF FIRE GASES

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TABLE III C  
VERTICAL PORCELAIN KILN. BURN ON THE 18TH OF MAY

Day.	Hour.	Details and observations.	Samples drawn 0.5 m. under the arch.		0.5 m. above the kiln floor.		In the middle flue of the biscuit kiln.	
			Per cent of air.	Per cent of air.	Per cent of air.	Per cent of air.	Per cent of air.	Per cent of air.
May 18	9	Beginning of firing 3 o'clock in morning	17.41	1.30	0.00	1.60	94	16.32
			0.4	0.0	0.0	0.0	178.7	16.2
			16.61	1.90	0.0	1.31	85	13.64
			1.30	0.2	0.0	1.31	80.00	12.68
			17.01	1.50	0.0	1.50	79.3	14.93
			1.50	0.0	0.4	0.63	30.00	177.5
			15.33	1.40	0.0	1.41	77.5	15.13
			1.4	1.01	1.4	1.41	577.4	16.5
			-	80	0.0	1.21	41.5	2.3
							86	0.4
							1.0	79.5
							91	91
P.M.								
1		Fireplace reduced to 50 x 32 cm.	16.71	1.60	0.30	0.01	679.5	96
			16.52	1.10	0.30	0.60	0.01	1.279.3
			1.10	0.30	0.01	1.2	91	16.03
			16.0	0.0	0.0	1.10	0.01	1.278.1
			0	0	0	0	0.01	1.0108
							17.4	1.3
							0.0	0.0
							1.1	79.2
							102	102
2		-						
3		-						
4		-						
5		-						
6		After the conclusion of the burn						

Porcelain bluish white, the blue decorations pure, only now and again slightly bubbled and sunk in.

marked porcelain, will result. According to the present determinations, which are confirmed by experiments made with kilns of other systems, that are used in the porcelain industry, this necessity does not appear, a fact which is to be well considered from an economic standpoint. If we take the averages from the foregoing tables we get the following percentages of air:

	0.5 m. above the kiln floor. Per cent.	0.5 m. under the arch. Per cent.	In the center fine. Per cent.	Average. Per cent.
Burn <i>a</i>	- - -		118	118
Burn <i>b</i>	- - -	77	74	75.5
Burn <i>c</i>	- - -	95	89	92

*i. e.*, in burn *a* the fire gases were oxidizing, since on an average 18 per cent more than is necessary for complete combustion passed through the kiln; in burn *b*, 24.5 per cent of the theoretically necessary amount was lacking; in burn *c*, 8 per cent; in the last two cases the kiln atmosphere was therefore reducing. In all three cases the quality of the white porcelain obtained was good, in *a* the color showed a yellowish tinge, in *b* and *c* a bluish tinge, the painting with cobalt oxide showing greater defects the more reducing the kiln atmosphere had been. It therefore seems as if for the production of white porcelain an excess of combustible gases in the kiln within certain limits and during the entire length of the burn, is not injurious, nor is it absolutely necessary, while for the most stable of the underglaze colors (the cobalt oxide) with strongly reducing gases an injurious effect is to be expected.

The yellowish or bluish tinges which the porcelain, made from the same body, takes in the fire, must be ascribed to compounds of iron which are never completely wanting in the raw materials used. The soft biscuit possesses for the most part a reddish or yellowish color which is to be ascribed to its content

of free oxide of iron; according to experiments<sup>1</sup> previously communicated, clays slightly colored by oxide of iron take on a gray color when they are heated at a light red heat in an atmosphere of reducing gases which vanishes again by a subsequent heating in an atmosphere high in oxygen, passing over into yellow with a high content of iron and into a pure white with a small proportion of iron. This change in color seems to be caused by a reaction of the silicates of alumina and the free silicic acid on the ferrous oxide formed in the reducing atmosphere, which on account of its pronounced basic characteristics, which the ferric oxide possesses in a much less degree, unites more readily with the silicates than the latter and passes over into pale yellow or white silicates of iron and alumina, while under similar influences the free iron oxide again obtains its red or brown color. This same process must also take place in the burning of porcelain, and according to the figures given in Table IIIa it seems as if it were sufficient for the production of white porcelain, that only in the first stages of the burn, before the beginning of the condensation of the body and the melting of the glaze, reducing influences make themselves felt for a time, and that an excess of oxygen later on in the burn cannot destroy the white color caused under these circumstances, in spite of the fact that the ferrous oxide again finds an opportunity of changing into the ferric oxide. Only in the case when the body during the whole course of the burn had no opportunity of coming in contact with reducing gases, but was burned in an atmosphere always containing an excess of oxygen, it seems to retain the yellow color of the biscuit. This yellow color must, however, not be confused with the brownish color which is given to porcelain by "smoke." This permanent yellow color can appear in such places at which a current of air penetrates through crevices in the kiln wall. This will take place especially at the peep-holes and openings for the taking of samples, especially if they are only closed by

<sup>1</sup> *Thonindustrie-Zeitung*, 1877, No. 3: "The Significance of the Continuous Kiln for the Clayware Industry."

simple glass or mica plates. This will explain also the phenomenon often observed that only the test pieces are yellow while the contents of the kiln are faultless. The opposite case cannot easily occur unless it be that a coloring of the porcelain has taken place by carbon set free by a vigorous reducing effect, passing beyond a certain limit. If there is only a slight excess of reducing gases in the kiln during the burning, the white color of the porcelain has a bluish tinge, which may perhaps be ascribed to the formation of a ferrous silicate, very high in silicic acid, while the silicates of the ferrous oxide low in silicic acid, as they may be formed in clays high in iron and low in silicic acid, produce a grayish blue color (stoneware) or a black color (clinkers). The experience that by the addition of quartz, greater transparency and a bluish color is given to the porcelain, finds its reason perhaps solely in this fact.

According to Table III $\alpha$ , and observations to be given later on, it does not seem at all advisable to maintain an excess of combustible gases in the burning of the porcelain, during the whole time of the burn. It should be our endeavor to obtain, as nearly as possible, conditions under which the air supplied just suffices to burn the fuel to carbon dioxide and water vapor, as the condition in which the greatest economy in fuel is to be expected. It might not be always possible from the practical standpoint to keep within these conditions. In a large kiln it is undoubtedly much more difficult with a neutral but short flame, to produce the very high temperature required uniformly throughout the whole kiln, than with a long flame not sufficiently fed with oxygen; and experience has taught that with a uniform flame, completely filling the kiln, and with a smoking chimney, in spite of the waste of fuel connected with it, the operation will always be much safer and less liable to a local overheating, than with a short, smokeless flame. Nevertheless, it will be important to keep in mind that for colored porcelains the best conditions for a successful burn are different from those of white porcelain, and that a management of

the kiln which affords safety for the latter may be far from sure for the production of colored porcelain. In this there are probably to be found the chief difficulties of the use of underglaze colors and hard porcelain body colors.

B. HORIZONTAL KILNS  
(Kilns with Horizontal Direction of Flames)

*4. Continuous Brick Kiln in Heegermühle*

The kiln differs but little in its construction from the ordinary Hoffmann continuous kilns. It is, however, rather short. The number of chambers is nine, 4 meters wide, 3 meters high, and 6 meters long; the number of fire-holes is twenty for each chamber, which are arranged in cross rows containing alternately two and three. The firing was done by means of an earthy lignite of low fuel value, from Freienwalde on the Oder, with the addition of one-fourth of Bohemian lignite. Since the amount of coal to be supplied is very large, on account of the low heating value, about 26 to 30 pounds per hole, the firing flues with their projections could not catch this amount and the larger amount of the fuel fell upon the kiln-floor. The firing took place in 8 rows of holes, one after the other, none being omitted. The bricks obtained were yellow, and yellowish green clinkers and hard brick almost free from efflorescence in the lower part; in the upper part, especially between the firing flues, the bricks were softer, common brick more or less red colored. The raw material was the same as that of the Heegermühle brick kiln first discussed.

In the manner of setting and firing there was no deviation from the ordinary procedure, except that twice a day the draft was reduced to a minimum for about half an hour, immediately after firing, just enough to prevent the smoke developed from passing into the portions of the kiln that were already cooling; when the smoke had disappeared the draft was cut off completely. This was done, partly to raise the temperature,

**TABLE IV**  
Continuous Brick Kiln in Hüttenmühle

Time	No.	Samples drawn 0.3 m. under the arch. 0.3 m. above the floor.	0.3 m. under the arch.		0.3 m. above the floor.	
			Per cent of air	Per cent of air	Per cent of air	Per cent of air
P.M. 3:35	3	Immediately after firing, feeble gray smoke	14.3	0.00.00.0	7.7	77.9
A.M. 5:05	4	Fire well burnt down, before firing	4.5	0.00.00.0	18.9	76.7
5:50	5	After firing and complete stopping of the draft	51.4	1.20.10.00.0	0.0	47.3
A.M. 6:20	6	Kiln still without draft, fire still clean	18.2	0.00.00.0	3.0	78.8
8:00	7	Ten minutes before firing, the fire advanced to 2 chambers above the place where the tests were taken	4.6	0.00.00.0	18.9	76.5
8:20	8	Immediately after firing, feeble gray smoke appeared	3.1	0.00.00.0	15.9	81.0
9:00	9	After the fire had well burned down	0.0	0.00.00.0	20.3	79.7
9:15	10	Immediately before firing	0.0	0.00.00.0	20.0	80.0
9:35	11	After the firing, the draft stopped, strong gray smoke	57.0	3.90.00.30.0	0.0	38.8
9:55	12	Valves still closed, but the thick smoke disappeared	51.0	0.80.10.00.0	0.0	47.1
10:30	13	Immediately after firing, gray smoke at the chimney	2.4	0.00.00.0	16.9	80.7
11:00	14	The fire burning down, $\frac{1}{2}$ hour before firing	0.7	0.00.00.0	17.6	81.7
P.M. 11:35	15	Immediately after firing After the fires had completely burned down, sample drawn in the middle of the chamber being fired	1.0	0.00.00.0	17.9	81.1
1:30	16	Immediately after firing	6.2	0.00.00.0	13.4	80.4
5:15	17	Fire well burnt down	0.4	0.00.00.0	19.2	80.4
5:45	18	After firing and stopping of the draft	45.3	2.10.00.00.0	0.0	52.7
6:10	19	Kiln free from smoke but still without draft	51.6	2.40.00.00.0	0.0	46.0
A.M. 6:30	20	Immediately after the firing, 2 fire shafts, behind place of sampling, fired	1.0	0.00.00.0	17.5	81.5
11:34	21	Fire well burnt down, chimney free from smoke	1.0	0.00.00.0	18.4	80.6
4:15	22	Immediately after firing, gray smoke	0.3	0.00.00.0	19.7	80.1
4:50	23	During the burning down of the fire	64.5	2.70.00.00.0	0.0	32.8
5:05	24	After the firing, draft stopped	53.7	1.50.00.00.0	0.0	44.8
5:30	25	Valves still closed	53.7	1.50.00.00.0	0.0	44.8

always low under the arch, under ordinary circumstances, and partly to make it possible to bring about those conditions which develop the natural yellow color also in the upper parts of the kiln, *i. e.*, bring about the action of a reducing kiln atmosphere.

The samples were taken from the kiln by means of two iron tubes, glazed on the inside by means of boric acid and sand, which were introduced through one of the doors into the empty space formed in the brick by the paper partition. They were so placed through the wall, closing the door-opening, that the tubes ended about 0.3 meter under the center of the arch and 0.3 meter above the floor of the furnace, about midway between two firing flues.

The samples were taken on three successive days at the same place in the kiln while the fire passed it. On the first day the sample was taken from the low fire, about 2 meters before the row of holes fired first; on the second day from the full fire; and on the third from the back part of the kiln, where the temperature had already begun to fall.

Table IV shows the changes in the kiln. As will be observed, the composition of the fire gases varies exceedingly according to the time that has elapsed after firing, according to the height in the furnace, and according to whether the samples were taken in the slow fire, in the middle, or at the end of the full fire. In general, a considerable excess of unburned gases is found along the kiln floor even immediately before a new charge of fuel, while under the arch there is always a considerable excess of oxygen available for combustion. After the low fire the differences are diminished by the gradual diffusion of the upper and lower currents of air and increased towards the rear of the full fire. When the draft is temporarily cut off an equalization takes place in so far as the oxygen contained in the kiln is entirely or almost consumed above as well as below and its place is taken by a usually only slight excess of combustible gases found under the arch. At the same time an extraordinary rise in the content of carbon dioxide is noted. This car-

bon dioxide cannot all have come from the combustion of the lignite; its origin must be looked for elsewhere. Since in combustion one part of oxygen furnishes exactly one part, by volume, of carbon dioxide and the atmospheric air contains 21 per cent of oxygen, the carbon dioxide formed in the fire gases, from combustion, can at most amount only to 21 per cent if pure carbon free from hydrogen (coke, charcoal), is burned. A rise in the content of carbon dioxide to 50 or 60 per cent, as was often noted, may have two causes: First, while the draft is shut off, in the continued evolution of carbon dioxide from the clay which contains 16 to 18 per cent of calcium carbonate in the raw condition; second, perhaps, in the supply of oxygen to the combustion, which has no connection with the atmospheric air. As such we may take the oxygen of the oxide of iron contained in the clay. That a large amount of oxygen is given off by the oxide of iron, and inversely that a large amount of oxygen is taken up out of the fire gas after a reduction, is very probable and finds its confirmation in observations communicated below, where a disappearance of oxygen compounds from the fire gases is observed much more strikingly after a reduction than in this kiln.

By cutting off the draft and the reducing atmosphere thus produced throughout the kiln, a vigorous evolution of gaseous sulphur compounds from the clay took place; the gases drawn from under the arch had an intense odor of sulphurous acid, those from the floor of the kiln, of hydrogen sulphide; with the usual manipulation of the fire only the gases drawn from the floor of the kiln had a sulphurous odor, at times of sulphurous acid and again of hydrogen sulphide.

#### *5. Brick Kiln of the Splau Clay Works, a So-Called Partially Continuous Kiln.*

The kiln possesses a burning tunnel about 10 meters long, 3.5 meters wide, and 3 meters high, which is covered with an arch constructed according to the line of a catenary; at the one end is a grate extending through the whole width of the kiln,

formed by narrow rods about 1 meter long with spaces about 5 mm. wide. Fuel can be supplied to this grate through three doors. At the other end of the kiln by the side of the door in the wall, two openings are arranged in the kiln floor capable of being closed by sliding dampers; by means of underground flues these apertures are in connection with a high chimney. Beginning 2 meters from the grate six slit-like openings are arranged in the arch at intervals of 1 meter. These openings may be closed by means of iron boxes whose edges dip into sand grooves on the platform of the kiln, and which serve to charge fuel into the burning kiln from above. The bricks to be burned were set with three floor flues, running through the whole length, 25 cm. high and 12 cm. wide, the bricks lying flat with spaces of 3 to 4 cm. Under the slits in the arch, firing slits were left in the setting; these slits had regular projections of bricks in every course in order to provide a support for the coal thrown in from above. The firing took place at regular intervals with measured amounts of fuel; at first a strong fire was built on the grate only. After the brick had begun to be dark red at the middle of the kiln, firing through the slits in the arch was also begun, and the number of slits fired was gradually increased. The fuel was supplied from above in measured quantities and always seven to ten minutes later than on the grate below. The product is a fine face brick of a yellow to a buff color, produced from lignite clays, free from lime, and belonging to the lowest class of fire clays.

The samples of gas were taken on the first day by means of iron tubes inserted in the slit in the arch nearest to the grate, at a horizontal distance of 2 meters from the grate, 0.1 meter above the floor, and 0.1 meter under the arch; on the second and third day the samples were taken through the door opposite the fire, simultaneously at a height of 1.5 meters and 0.3 meter above the floor, and 0.8 meter under the arch.

Table V contains the results of the investigation. Sum-

ming up the similar moments and taking the averages, we obtain the following account of the burning process :

	Air under the arch. Per cent.	Air at the floor. Per cent.
1. Fired only from the grate; grate completely covered with coal:		
a. Immediately after firing - - -	114	82
b. Fire burned down completely - - -	286	264
2. Fired only from the grate; grate bare about 10 to 15 cm. in the rear:		
a. Immediately after firing - - -	147	365
b. Fire burned down completely - - -	496	1120
3. Fired through four slits only, immediately after firing - - -	98.5	93.5
4. Fired from the grate immediately after firing through the slits:		
a. Immediately after firing - - -	91	33
b. Fire burned down completely - - -	103	91

As may be seen from these figures the distribution of the combustible gases arising from the decomposition of the fuel and of the atmospheric air supplied for combustion, is by no means uniform. With the usual regulation of the fire (*i. e.*, when the grate is covered as evenly as possible with fuel), there is, even immediately after firing, a larger amount of atmospheric air present in the upper parts of the kiln than is necessary for combustion; in the lower parts, on the contrary, a lack of air and, therefore, direct loss of fuel appears. The combustible gases below are not utilized later. When the samples were taken during the first two days no red heat was visible at the points in question, and a mixing of the upper and lower currents could therefore take place only in a part of the kiln, in which the temperature was so low that ignition was impossible. If, on the other hand, a part of the grate remains uncovered in the rear, together with a large increase in air, the opposite case will arise so that the lower part of the kiln becomes richer in air. The admission of air behind the fire may often become the means of avoiding these irregularities and preventing the escape of the unused gases to

the stack, especially during the latter part of the burn when the unburnt gases along the kiln floor increase still more in quantity.

After firing through the slits in the arch alone, the composition of the fire gas is almost entirely uniform, although even here a somewhat greater reducing effect is noticed in the lower part. This improved proportion, as compared with the continuous kiln previously discussed, is probably to be ascribed solely to the circumstance, that here in the firing slits far more points of support are given than in the shafts of the former, and that therefore a smaller part of the fuel which also is of better quality dropped to the floor of the kiln. An extraordinarily large excess of unburned gases appeared along the floor of the kiln after firing the grate when the slits had just been fired.

Through these inequalities in the composition of the fire gases the face brick in the kiln are exposed to quite different influences. In the upper part of the kiln there may be noticed a continuous fluctuation between reducing and oxidizing influences from one firing to another; in the lower part, however, at least in the period of the strongest fire, there is only a reducing condition, since here even before a new charge of fuel no excess of air is present. This difference is shown in the appearance of the burned bricks. While the larger part of the kiln contents has a brownish so-called buff color, varying within very few shades, according to the higher or lower temperature, the lower parts of the kiln possess a more reddish color, and at the same time show a weak luster owing to a very thin glaze. The latter seems to have come from a vaporization of alkalies from the ash of the fuel.

A number of the analyses shows a very peculiar phenomenon in the proportion of indifferent nitrogen to the products of combustion and the unused oxygen which was already indicated in discussing the figures observed in the Heegermühle continuous kiln. These are the samples taken on the morning of the 4th of November at 10.50, 11.20, 2.55, and 3.25 in the upper part of the kiln.

TABLE V.—Semi-Continuous KILN OF THE SPLAU CLAY WORKS

		at 0.3 m. above the floor.		at 0.3 m. below the arch	
		Oxygen	Nitrogen	Oxygen	Nitrogen
P.M.	3.50 Before firing	-	-	12.3.1.2.0.4	0
	4.05 Ten minutes after firing	0	0	4.8.0.7	0
A.M.	4.20 Shortly before a new fire	0	0	13.4.6.6	0
	4.35 Immediately after firing	0	0	13.5.3.0.1	0
P.M.	5.00 Immediately after firing	0	0	12.7.2.5.7.0.5	0
	5.20 Fire burnt low upon the grates	0	0	12.8.1.2.7.5.3	1.4
	5.35 Immediately after firing; grate in the rear portion left uncovered in a narrow strip	0	0	10.0.1.3.2.7.8	0
	6.00 Immediately before new firing	0	0	14.3.8.0.1	0
	6.30 Immediately after firing; rear grate left uncovered as above	0	0	3.0.4.3.0.1	0
	6.45 Fire burnt down low; at the test-hole 2 meters from the grate a just visible red heat	0	0	14.8.1.9	0
No. 3 10.40	After firing, tests taken in rear kiln door, no visible heat	0	0	5.0.8.0.0	0
	11.10 Immediately after firing	0	0	5.0.8.3.3	0
A.M.	11.20 During the burning down	0	0	4.0.8.0.0	0
	6.25 Fire burnt down low before the firing	0	0	5.7.8.3.1	0
P.M.	6.43 Immediately after the firing	0	0	13.0.8.0.8	0
	6.55 Ten minutes before firing	0	0	2.1.8.1.6	0
	7.15 Immediately after firing	0	0	10.9.15.0.4.0	0
No. 4 9.45	o bottom, 15 minutes after firing after firing through 4 holes in arch, fire on grates burnt down	0	0	13.1.15.4.0.9	0
A.M.	10.00 Immediately after firing through 4 holes in arch, grate fires burnt down	0	0	1.7.8.4.5	0
	10.30 Immediately before new firing thro' arch and grates	0	0	10.8.10.8.3	0
P.M.	10.50 Immediately before new firing thro' arch and grates	0	0	1.9.8.1.8	0
	11.20 Immediately after new firing thro' arch and grates	0	0	10.0.11.9.1.4	0
	11.40 Immediately after firing grates, 4 arch holes fired 7 minutes earlier	0	0	0.6	1.3
	2.40 Immediately after firing the grates and 5 arch holes	0	0	0.6	1.9
	2.55 Immediately before firing, chimney free from smoke	0	0	0.6	1.9
	3.10 After firing 5 arch holes and the grates	0	0	0.4	0.3
	3.25 Immediately before a new fire	0	0	0.4	0.3

A decrease in the nitrogen content of the fire gases below the content of nitrogen in atmospheric air can take place by a mixing with products of the distillation of coal, and is, therefore, not strange; on the other hand a considerable increase above the nitrogen in the atmospheric air is less easily explained. When pure carbon burns in atmospheric air, say charcoal, there is formed from every part by volume of oxygen used one part by volume of carbon dioxide. The proportion of nitrogen, therefore, remains unchanged, and since the air contains 21 per cent of oxygen if no other sources for the formation of carbon dioxide are present (for example, the heating of calcium carbonate), the sum will be: carbon dioxide plus oxygen equals 21 per cent. This proportion is changed somewhat when the fuel contains more hydrogen than corresponds to the oxygen, also contained in it, required for the formation of water; this surplus is then likewise consumed by the oxygen of the air. This takes place with the most of the fuels used, wood, lignite, coal, etc. The amount of this free hydrogen is, however, always small and the analysis can, therefore, give values for the sum of oxygen and carbon dioxide but little smaller than 21 per cent and correspondingly larger ones for the nitrogen.

If we examine the foregoing as well as following analyses that show complete combustion, we will, therefore, find that in the majority the sum of oxygen and carbon dioxide fluctuates between 19 and 21 per cent, and only in a few goes down to 17 per cent. In the cases discussed here, however, this sum goes down to 12.5, 8.5, and 9.9 per cent respectively. This striking fact caused the immediate repetition of the determinations, but the same result was obtained. Such a drop cannot be explained by the great hydrogen content of the fuel, not even if the fuel were illuminating gas, which is richest in hydrogen; such an explanation would, however, also prove insufficient if we consider that the samples in question were taken when the fire had burnt down altogether and the hydrogen compounds of the fuel had already been decomposed and carried away.

An absorption of the carbon dioxide from the fire gases on the part of the constituents of the clay cannot be expected at this high temperature, and there remains, therefore, only the explanation that a removal of oxygen has taken place. This explanation is raised to evidence if we consider the figures preceding those above mentioned. A vigorous reducing action of the fire gases always preceded the phenomenon which occurs when the fire was burnt down. The disappearance of oxygen cannot be ascribed to a deposit of soot since then a like volume of carbon dioxide would have been produced in place of it. On the other hand, the iron content in the clay explains the increase in the proportion of nitrogen in the fire gas by absorption of oxygen. Free iron oxide may be decomposed by the constituents of the fire gases, carbon monoxide, hydrocarbons, and hydrogen even at a dark red heat and all the more easily the looser and more finely divided it is. The action takes place in this way : oxygen is withdrawn from the ferric oxide which burns the carbon monoxide to carbon dioxide, the hydrocarbons to carbon dioxide and water vapor, and the hydrogen to water vapor ; the ferric oxide is changed to an oxide low in oxygen, the ferroso-ferric oxide, or ferrous oxide, or into metallic iron. The metallic iron arising at a comparatively low temperature, far under its melting-point, forms a black spongy mass which can be kept unchanged only when the air is completely shut off. As soon as it comes in contact with air it ignites of its own accord and burns again to ferric oxide by taking up oxygen. This effect must, however, take place before the ferric oxide, of which over 3 per cent were contained in the clay in the case before us, is chemically united with silicic acid and only admixed mechanically. Accordingly the ferric oxide of the clay can take a lively part in the process of combustion in so far as it furnishes a part of the oxygen wanting for combustion when the air supply is insufficient, taking on this oxygen again as soon as there is an excess of air, so that it furnishes a reservoir for oxygen, so to speak. That this participation in the combustion is considerable is indicated

by the fact that half and even more of the entire oxygen content could be withdrawn from the air passing through the kiln; a like amount must, however, have been given off by the ferric oxide in the preceding period of reduction. From the composition of the gases during the period of reduction we cannot find directly whether the combustion has taken place at the expense of the oxygen of the air, or also at the expense of the ferric oxide of the clay, since the amount of carbon dioxide which in very many cases is greater than  $\frac{1}{7}$  of the nitrogen may also have been increased by the production of carbon dioxide as a product of the distillation of coal.

#### *6. Stoneware Kiln of Joseph Schult, in Hoehr*

The kiln which serves for the burning of the pearl-gray salt glazed Koblenz stoneware colored blue with cobalt has the construction very common in the so-called Kannenbaeckerland as it has been used there for centuries. The kiln space, oblong in outline, is about 6 meters long, 2 meters wide at the bottom, and 2 meters high. The profile of the arch forming the kiln space is that of a raised ellipse. In the kiln arch, which is accessible from the outside by a gallery formed by masonry, two-thirds as high as the kiln, there are twenty-seven round openings uniformly distributed in three rows which serve as vents for the products of combustion and can be closed, more or less, by clay tiles laid on top. The two series of holes on the long sides serve at the same time for the drawing of trials and throwing salt into the kiln and have for this purpose branches leading horizontally outward, immediately above the arch, which are generally kept closed by means of tiles placed in front of them. The bottom of the kiln is formed by a number of arches which have spaces, 10 cm. wide, throughout the whole width of the kiln and which cover the flue, 0.5 meter high, extending through the whole width and length of the kiln. On the one end of the kiln there are three fireplaces provided with iron grates, doors, and ash pits, each 1 meter long and 0.5 meter wide, below the kiln space and separated from it by the perforated arches. At

the opposite end is the door ; after closing it an opening is also left here for the exit of the flame, about 15 cm. in diameter, to cause the flame to come up to the door. The fire from the grates is distributed below the whole floor of the kiln through the flue, rising somewhat towards the rear, and passes into the kiln space through the slits which are left between the arches forming the floor. In order to be able to break and distribute the fire better these slits in the kiln floor are covered with burnt clay blocks 3 cm. thick and about 15 cm. long, similar to a grate. The construction is thus not exactly that of a horizontal kiln, but that of a link between the vertical and horizontal kiln in which the direction of the flame is at first a horizontal and then a rising one. The dry ware is set without saggers, only with the help of clay plates, rings, and wads that are cut from stiff clay. The kiln was fired with wood only, and for three days; the fire is gradually increased until a strong shrinkage of the ware is noted and a test, made by throwing salt on small vessels under the arch or perforated test sherds, indicates the temperature at which the salting can take place. By covering and opening the holes in the arch for a time the flame is so regulated that the heat is uniformly distributed in the kiln. When the correct degree of heat is attained the fire is kept burning briskly and the salt introduced by two workmen, each on one side of the kiln, through the salt holes in the arch by means of long iron ladles and scattered over the ware. The salting is done twice at intervals of half an hour, using 100 to 120 kg. of denatured commercial salt.

The samples of gas were taken in the last hours of the full fire and during the salting by means of clay tubes, 0.75 meter long, reaching through the salt holes some distance under the arch ; the samples were taken at both ends of the kiln, simultaneously, in the first salt hole over the fireplace and in the last one at the door of the kiln. After each supply of wood to the grates a dense black smoke came from the openings which was colored less intensely at the fireplace end and vanished sooner than at the opposite end.

The results of the analyses are contained in Table VI.

If we neglect the last salt fires in which there was a more frequent opening of doors on account of the frequent supply of wood, we get as the average of the air supply during the observed period of full fire:

	Above the fireplace. Per cent.	At the door end of the kiln. Per cent.
Immediately after firing	85.5	63.5
Fire burnt down	152.5	99.5

We see that in the part of the kiln opposite that of the fireplace a much stronger outflow of unburnt gases takes place and that while the fire burns down a very considerable quantity of excess air appears above it.

#### 7. Stoneware Kiln of William Zoeller in Grenzhausen

This kiln has the same construction and dimensions as the one just discussed, but serves for the burning of mineral water jugs in which not a pearly gray color of the body, but a yellowish brown, is desired by the consumers. The clay used contains some iron, and in its raw state has a pale rose color. According to the observations made the desired yellowish brown color of the jugs, which extends only to the surface while the interior of the body is bluish-gray, is said to be produced by setting the ware more loosely and keeping the slits in the bottom of the kiln more open than is the case with the gray stoneware.

The samples were drawn exactly as in the preceding kiln. During the taking of the samples the heat at the door end was diminishing; therefore, to increase the fire, the smoke and salt holes above the fireplace and in the middle of the kiln were covered, and only those at the door end opened, the draft here being increased by means of pipes set up on end. The salting of the kiln, which takes place with closed fire doors, was performed about eight hours after the taking of the samples. The firing was done with coal with the addition of some billets of cord wood.

TABLE VI  
STONWARE KILN OF JOSEPH SCHULZ, AT HOMER

At the door end of the kiln.		In the arch of the kiln over the fireplace.	
		Per cent of	Per cent of
Nitrogen.	Oxygen.	Nitrogen.	Oxygen.
1.60.64.1	76.5	96.14.5	8.2.0
0.0	8.6	80.4	166.16.0
2.21.40.7	74.8	75.14.8	6.1.0
0.0	6.0	80.5	139.16.0
10.3.0	3.8	79.9	107.16.7
0.0	5.4	80.2	129.16.7
	0.5.7	80.2	136.11.4
			1.00.8.0
			0.7.4.79.4
			1.26
Hydrogen.	Hydrogen.	Methane.	Methane.
Hydrogen.	Hydrogen.	Hydrogen.	Hydrogen.
Heavy hydrocarbons.	Heavy hydrocarbons.	Light gas.	Light gas.
Carbon monoxide.	Carbon dioxide.	Carbon dioxide.	Carbon dioxide.
Hydrogen.	Nitrogen.	Nitrogen.	Nitrogen.
Hydrogen.	Oxygen.	Oxygen.	Oxygen.
Methane.			

Table VII contains the results of the analyses. The burn, the results of which in spite of the great differences of temperature at the beginning were entirely normal, can serve as an example to show what the conditions are, when, by damping the flame at one end of the kiln, the fire is driven to the other end. While the atmospheric air which penetrates through imperfections in the fireplace seems to seek the nearest way out of the kiln, the fire gases high in carbon and hydrogen pass along the bottom to the end of the kiln where they rise; but when the fire has burnt down completely, a greater uniformity in the composition of the gases seems to appear. While immediately after firing half of the combustible products of the decomposition of coal escape unused, still in the rear part of the kiln even above the fireplaces, the amount of oxygen passing in is considerably larger than would be necessary for economic combustion.

*8. Kiln for Common Faience Ware of Gottfried Schoeffel & Son, in Berlin*

The kiln is a so-called "potter's long kiln" fired with wood. It has an oblong shape, is 4.5 meters long, 1.9 meters wide, 1.6 meters high, at the center of the flat arch. In one of the front walls there are three open fire-holes of which the middle one is 40 cm. square and the two latter 25 cm. square. The wood cut in lengths of 50 cm., burns in these fire-holes without grates. Before the fireplaces there is a combustion chamber, 50 cm. wide, extending through the whole kiln, which is formed by a perforated fire-wall built of fire-bricks, reaching close to the arch of the kiln. On the opposite end is the door and in its arch the opening to the chimney flue. The kiln has no so-called vault, but the fire leaves through a slit, 12 cm. wide, extending across the entire arch in the back wall which gradually contracts to a chimney, about 50 cm. in diameter and 20 meters high, serving for two kilns lying side by side; through this chimney the heat of the cooling kilns is conducted to the workshops. At a height of 12 cm. above the floor of the kiln a second hearth is formed from bricks, placed on end, and fire-clay tiles under which,

TABLE VII  
KILN OF WILLIAM ZÖLLER AT GRENZHAUSEN

throughout the whole length of the kiln and corresponding to the fireplaces, there are three firing flues, 12 cm. wide, which may be compared with the arches of an up-draft kiln. Immediately behind the fire wall there is a tier of waste stove tile; in the remaining part of the kiln there are stove tiles, half glazed and half green for biscuit burning as well as ornaments. The green ware is set in courses with clay props on fire-clay tiles, without the use of saggers, so that the glazed tiles are placed in the middle and the lower part of the kiln, the unglazed in the extreme rear and upper courses. The clay used for the production of these tiles is that of Velten, near Berlin, much used for this purpose. The glaze is an enamel fritt made from tin and lead ash, sand and common salt, which produces a pure white opaque layer on the yellow burning clay containing about 30 per cent of calcium carbonate and 5 per cent of ferric oxide. A burn requires about thirty hours. In the first hours a small fire is kept only in the middle fire-hole; this is gradually increased and after six hours fire is placed into all three fire-holes which are now open. At the full fire the holes are completely filled with cord wood which is allowed to remain until it is burnt down to coals. When the fire is burning down, the upper part of the fire-holes is so covered up with iron plates which rest on brick that the air can get to the wood only through an opening 12 cm. wide. In proportion as the heat progresses along the floor of the kiln the stoking passages under the double hearth are charged at every fire with sticks of wood. At the end of the burn the entire combustion chamber is filled with pieces of cord wood placed in an almost upright position, split quite thin, and besides the fire-holes are filled with wood in order to cause as brisk and intense a fire as possible.

The samples were taken in two burns by means of porcelain tubes which were so introduced through the door in the rear part of the kiln that they extended 1 meter into the kiln and ended 0.1 meter under the arch and 0.1 meter over the double hearth of the kiln. The corresponding samples were, as heretofore, taken from the kiln simultaneously.

FAIENCE KILN OF GOTTFRIED SCHOEFEL & SON, BERLIN.  
TABLE VIII.  
FAIENCE KILN OF GOTTFRIED SCHOEFEL & SON, BERLIN.  
BURN ON THE 29TH AND 30TH OF JUNE

		Sample drawn 1 m. back in the kiln and 0.1 m. beneath the arch.		0.1 m. above the double floor.				
		Oxygen.	Nitrogen.	Oxygen.	Nitrogen.			
29	10.45	Water smoking fire, only in the center fire-hole. Sides closed, samples have been drawn just after firing	2.2 0.1 2.8 0.1 3.9 0.1	17.9 79.8 17.3 79.8 16.0 80.0	619 2.0 525 2.0 396 2.6	0 0 0 0 0 0	0 18.0 0 18.1 0 17.3	80.0 654 79.9 677 80.1 590
	11.13							
P.M.	12.00	Middle fire-hole well filled up when firing	2.8 0.0 15.2 1.00 16.9 1.30	0 0.2 0 0.3 0 0.4	17.3 79.9 86.4 107 1.1 79.9	1.6 0 12.1 0.3 93 15.2	0 0 0 0 0 0	18.5 79.9 65.5 77.6 2.2 81.3
1.00		Samples drawn immediately after throwing in wood	0.6 0.1 0.6 0.1 0.6 0.1	0 0 0 0 0 0	1.9 86.3 2.3 78.6 4.2 79.1	12.7 0.2 11.5 3.3 9.7 1.5	0 0 0 0 0 0	5.8 81.3 7.3 73.6 9.0 76.7
5.30		All three fire-holes fired. Samples drawn just after firing	18.4 0.2 16.5 0.2	0 0 0 0	109 79.1 124 9.7	0.2 0.9 0.9 0	0 0 0 0	89 78.9 89 74.4
6.30								
A.M.	7.10	After filling up the fire-holes	11.2 0.0 4.9 0.0	0 0 0 0	9.2 79.6 78.1 550	17.6 20.0 7.2 0	0.1 0 0 0	4.2 75.7 13.5 79.3
7.30	8.00	Fires burnt down to glowing charcoal	-					126 726 278 278
10.00		Immediately after charging the fines and filling up the fire-holes	10.2 0.0 10.35 0.0	0 0 0 0	9.5 80.3 180 20.6	1.3 0.1 1.3 0.1	0 0 0 0	96 77.6 96 79.2
		Fires burnt down low; immediately before putting on a fresh baiting	5.6 0.0 19.0 1.40	0 0 0.6 0	15.0 79.4 105 75.6	345 2.6 216 9.6	0 0 0 0	740 18.2 78 3.2
P.M.	12.50	Immediately after replenishing the fire	7.8 0.0 13.5 0.80	0 0 0.20	11.5 80.7 4.1 79.2	216 4.5 115 21.7	0 0 0 0	78 67.4 24 85.9
1.00		Fires burnt down low	8.5 0.0 8.5 0.0	0 0 0 0	80.7 10.8 207 10.8	207 9.7	0 0 0 0	48 0.0 48 59.0
1.20	1.45	Immediately after replenishing the fire	-					48 2.9 114 87.4
		Fires burnt down low; the end of the barn						

## COMPOSITION AND ACTION OF FIRE GASES

FAIENCE KILN OF GOTTFRIED SCHÖFFEL & SON. BURN ON THE 5TH AND 6TH OF JULY

Day.	Hour.	Details and observations.	Sample drawn 1 m. back in the kiln and 0.1 m. under the arch.										
			Side					Bottom					
July 5	2.30	Middle hole fired with knotty wood. holes walled up	7.1	o	o	12.7	80.2	4.6	10.9	79.4	12.8	80.5	320
	7.00	Side wood. firing	14.8	0.1	o	o	5.7	79.5	2.0	2.0	0.1	5.9	131
	7.35	-	12.4	0.1	o	o	8.0	79.1	0.1	0.1	0.1	16.2	137
	7.50	-	5.4	o	o	o	15.5	79.6	9.4	9.4	0.1	9.8	687
	8.00	-	14.0	0.1	o	o	6.3	79.3	11.5	11.5	0.1	7.7	182
	9.00	-	13.3	0.2	o	o	7.2	79.1	5.9	5.9	0.1	14.2	301
	9.50	-	6.4	o	o	o	14.5	79.1	-	-	0.1	79.9	-
July 6	4.30	-	11.1	o	o	o	9.4	79.4	21.3	1.8	0.2	0.4	95
	9.50	Side fine scant	13.4	o	o	o	7.0	79.6	21.9	2.3	0.6	1.0	92
	10.10	-	6.9	0.1	o	o	13.9	79.1	3.8	o	o	16.6	482
	10.30	-	12.8	o	o	o	7.5	79.7	20.0	2.1	0.8	0.4	87
	12.30	-	4.9	0.1	o	o	15.8	79.2	3.0	0.1	o	16.7	482
	12.55	-	16.6	0.9	o	o	2.4	80.1	18.6	9.9	0.1	60.6	45
	1.10	-	16.0	0.2	o	o	4.5	78.6	22.3	10.8	0.1	54.3	324
	1.25	-	21.1	2.6	0.3	1.4	0.7	74.0	-	-	-	-	-
	1.40	-	16.7	2.7	1.0	0.6	3.0	76.0	19.1	5.1	0.1	70.0	-
	2.10	before	3.4	o	o	o	17.7	78.9	3.2	o	o	16.3	427
	2.30	closed	8.2	o	o	o	12.3	79.4	10.2	o	o	10.3	203
	2.55	ilm	5.5	o	o	o	14.9	79.6	337	5.6	o	14.5	314

The composition of the samples may be seen from the Tables VIII $a$  and VIII $b$ .

We note here the same phenomenon which was observed in the horizontal kilns previously discussed, namely, that under the arch there is nearly always a greater amount of free oxygen or, as the case may be, a smaller reducing effect than in the lower parts of the kiln. Only after the fire is well burnt down, that is, when the strong evolution of flame has ceased and the charcoal formed is glowing, is there an approach to uniform composition. Frequently also the case is reversed. The differences in the composition of the fire gases above and below are at first scarcely noted with a small fire and low kiln temperature, but become greater and greater in proportion as the temperature rises, the draft in the chimney increases, and the fuel supply is increased. Only in the intense fire at the end and not always even then does the oxygen in the upper region of the kiln vanish completely and make place for a reducing atmosphere; at any rate, the amount of unused combustible gases, even during the intense fire, is much larger in the lower part of the kiln than under the arch. If from the two tables showing the composition of the gases after an intense fire we take the average figures, we obtain for the supply of air:

	Per cent.		Per cent.
Under the arch - - -	104	Over the hearth - - -	54

*i.e.*, under the arch that point is approximately maintained at which complete combustion takes place, while over the hearth not more than half of the air required for combustion is present.

Like all calcareous clays the Velten clay frequently does not develop the yellow color in its purity, but the tiles or ornaments made from it are flashed red more or less. According to practical observations this takes place with special frequency in the upper courses. Since the yellow color develops only under the influence of alternately oxidizing and reducing conditions, this appearance of red spots under the arch is explained by the fact that according to the direction which the gases must

take through the accidental setting of the ware, reducing influences can appear but seldom under the arch and in some places not at all. The color of the glaze also seems to be affected very much by the varying composition of the fire gases.

Aside from accidental defects to be looked for in the clay body, not all tiles covered with the same enamel come from the kiln with the same color, and though, if seen by themselves they appear to have a pure white color, notable differences appear if we place tiles, from the same burn but from different parts of the kiln, side by side. The white color at one time has a pink tinge, sometimes a blue, green, or yellow tinge. From every burn, therefore, the tiles showing the same shades must be carefully selected. The more or less yellowish color is essentially dependent on the greater or less purity of the raw materials used for the production of the glaze and the care which is used in its preparation. But with the greatest care it cannot be avoided that the color of the glaze sometimes takes on a reddish tinge, and sometimes a green or blue. Judging from practical experience the glaze in the upper parts of the kiln seems to be inclined to the red, in the lower to the green, and between them there is a zone that furnishes the purest white perhaps by compensation of the almost complimentary colors. Since, as a rule, the same glaze is represented throughout the kiln, this difference of colors or shades can be ascribed only to the different influence of the fire gases. The influence of the impurities of the raw materials present in minimum amounts, which cannot be removed (as for example, a small amount of copper, cobalt, and manganese in the lead and tin that are used in the production of glazes), on the color, must be left to further investigations.

It is frequently assumed that lead and tin glazes cannot come in contact with reducing gases without being decomposed, because these metals are easily separated from them in a pure form. This, however, does not seem to be the case at all times, for in the above-named burns, especially in the finishing fire, reducing gases were present in very large amounts, especially in the

lower parts of the kiln, without injuring the ware; on the contrary, a reduction seems to have a favorable effect on the production of a pure white color of the enamel. It seems only necessary that a return of the regular metals to oxides be made possible by a sufficient supply of air after the reduction has taken place; and from this it is clear why the enamels of common faience ware are less exposed to damage in the open fire if impurities through ashes are avoided than when burned in saggers where, on account of the more difficult circulation of the air, the reoxidation is not so easy.

To be sure, circumstances may arise under which a reoxidation is prevented in the open burn and in consequence the glaze takes a gray to a black color; the ware is then called smoked. From smoke, that is from soot or carbon, this black color cannot come since the latter can not exist in the liquid lead glaze without decomposing the lead oxide. The black color is rather to be ascribed to finely divided particles of metallic lead or tin separated out in the glaze, which sometimes contract to larger drops and then produce round or ring-shaped spots in the glaze when again dissolved. As experience shows, smoked tiles are found chiefly in the lowest course over the hearth, especially when the charcoal had not completely burnt before closing the kiln, or when burning wood is still present. In the burn in question the thoroughly glowing charcoal in the hearth was almost completely burnt, excepting a few small fragments, when the kiln was closed.

The last two analyses of Table *VIIIb* show the composition of the fire gas after the complete closing of the kiln and an hour later. We observe that after the kiln is closed there is a considerable decrease in the amount of oxygen produced by the burning of the remnants of the coals. If the amount of charcoal is considerable it is reasonable to suppose that the oxygen of the stagnant atmosphere in the kiln is not sufficient to burn the coal to carbon dioxide, but gives rise to the formation of carbon monoxide which may remain in the kiln until the glaze has

cooled so far as to become solid, enclosing the lead or tin separated out by the carbon monoxide and protecting it from a reoxidation. With a sufficiently high temperature and with access of air, the black color of the glaze disappears again, for it is a well-known fact that smoked tiles may become white by reburning them.

Here, too, we find the phenomenon of the disappearance of oxygen from the fire gases following a strongly reducing effect, in Table VIIIa, in the samples taken below at 1 o'clock and at 1.45, which point to an energetic activity of the ferric oxide in the clay in regard to combustion.

### C. DOWN-DRAFT KILNS

#### 9. *The Stoneware-Pipe Kiln of Peter Simon Gers, in Hoehr*

The kiln has an oblong shape, is 5 meters long, 3 meters wide, and 2.75 meters high. In the enclosing walls of the two long sides there are four inclined grate furnaces, 0.4 meter wide and 1 meter high. The fire produced on these rises behind two fire bridges running along the whole interior length of the kiln, on both sides, and extending close up to the rather flat kiln arch. The exit of the fire gases is in the kiln floor, which is perforated and lies over a system of parallel flues which conduct the gases through a collecting flue to a stack about 20 meters high. The inclined grates were fired with coal, and care was taken not to clean them much during the burn so that a considerable layer of ashes accumulated on them. The fireplaces were closed by filling the space above the upper step with coal. In firing, which was done every twenty-five or thirty minutes, the coked pile of coal closing the hole was shoved onto the grate by means of a scraper and the opening covered with fresh coal.

During the salting the grates were kept as full of cord wood as the kiln could take up the flames arising from it, and the salt was thrown with a shovel into the fireplaces, hence only the salt vapors reached the kiln.

The samples were taken in the closing wall of the door in

TABLE II  
STONEMAKER-PETERSON PAPER MILK OF SIMON PETER CHURCH, IN HOKKA

one of the front walls of the kiln by the insertion of clay tubes 0.75 meter long, which extended 0.5 meter into the interior, 0.2 meter under the arch, and 0.6 meter above the floor of the kiln. The material for the production of the pearl-gray pipes is the same as that used in the kiln of Joseph Schult already discussed. The pressure conditions were such that under the arch, smoke came from the cracks in the wall, while in the lower part air was drawn in from without; after a last strong wood fire during the salting, strong flames and smoke came from all the cracks.

The samples taken at two different times are shown together in Table IX.

As we see, differences in the composition of the fire gases are scarcely noticeable, be the samples taken before or after the firing, only in the lower part of the kiln the excess of air always appears somewhat larger, which is explained by the fact that the walls of the kiln were not air-tight, and therefore admitted atmospheric air. This uniformity is doubtless due to the circumstance that no cold fuel was thrown upon the grates in firing, but only such that was ignited and burning so that no temporary disturbance of the burning process is caused by the strong cooling of the fire-box. For this reason no smoke from the chimney could be observed on the first day. Smoke appeared only in the last period of the burn, during the glazing, on account of the production of salt vapors, with a very great evolution of flame. The reducing effect is very intense since at times only half of the amount of air necessary for combustion was observed. Whether so great an excess of unburned gases is necessary during the salting or only gives an assurance of a good burn, giving to the ware the desired grayish white color, seems doubtful according to the observations which have been made with the same raw material in the stoneware kilns mentioned under 6, and further investigations would seem very desirable.

10. *Kiln for the Burning of Terra Cotta Ware of E. March's Sons in Charlottenburg*

The kiln in which the experiments were made is a two-story round kiln built according to the well-known Bosch system. It is about 4.5 meters in diameter and 3 meters high in its lower story. It is supplied with six fireplaces which are distributed in pockets in the outer circumference. The fireplaces form square shafts 1 meter deep, without grates, of which the lower half of one side is a grating of fire brick which allows the air to enter and at the same time permits the withdrawal of the clinkers without tearing out the coke. The shafts are filled from above and covered by a fire-clay tile. The outlet in the upper part of the fireplaces conducts the fire into the kiln at the floor and allows it to rise behind bag walls 0.6 meter high all around the kiln wall, allowing the flame to escape through narrow slits. The flame which rises to the arch and then descends again, is drawn off by a number of openings which are distributed in the floor of the kiln and are connected with the flues in the kiln walls that lie between the fireplaces, and conducted into the upper part of the kiln. The gratings of the fireplaces are put in only at the beginning of the fire, for during the water-smoking the coal burns without grates in the fireplaces bounded by walls on three sides so that a current of air enters the kiln above the coal.

In the first of the burns observed yellow terra cotta ware was burnt in the lower kiln at the beginning of white heat from a somewhat refractory clay free from lime; the ware was placed in large, walled boxes of fire-brick in order to protect it from the direct contact with the fire-gases. With the escaping heat, red terra cotta was burnt in the upper kiln without being protected. In the second burn only red terra cotta ware was burned in the lower part, without protection, at a bright red heat. The samples were taken during the first burn in the lower kiln, 0.5 meter under the arch and 0.5 meter above the kiln floor through a porcelain tube extending 1 meter into the kiln

through the wall of the door and at the same depth in the upper kiln; in the second burn, gas was drawn only from the two places designated in the lower kiln.

If we take the average figures from the two adjoining tables, Xa and Xb, in order to determine not only the average distribution of the fire gases, but also the deviations in the composition which arise through the periodic supply of the fuel, we obtain the following values for the air supply during the first burn:

	Lower kiln.		Upper kiln.
	Near the floor.		Under the arch.
	Per cent.	Per cent.	
Water-smoking	414	416	437
Immediately after firing	117	102	118
Before firing	213	214	223
In the case of the second burn, immediately after firing	134	133	—
Before firing	245	212	—

As we see from this with all the differences of conditions, which must necessarily arise through accidental circumstances in the treatment of the fire, the average composition of the fire gases is nevertheless a very constant one as far as the various kiln heights are concerned. In the first burn the aim was to produce a higher temperature and therefore the firing was more intense; in the second burn the smoking of the chimney was to be avoided as much as possible, since experience has shown that the newly set red terra cotta ware easily loses its fresh color by strong smoke and takes on a brownish tint.

Even though the smoking of the kiln was not altogether prevented in the second burn, yet we see that the composition of the fire gases, after the supply of new fuel, has still not reached the limit at which the oxygen of the entering air is consumed and reducing gases appear in its place, in the most cases on account of the smaller amounts of fuel. Only in a few cases was this

limit exceeded. In the first stage of firing, the water-smoking, where a considerable excess of air (more than four times the amount theoretically necessary) was noted, the fire gases showed always a small content of carbon monoxide, and at the same time almost constant moderate smoking; this is explained by the fact

TABLE  
TERRA COTTA KILN OF E. MARCH'S SONS, CHAR-

Day.	Hour.	Details and observations.	Lower kiln.						
			Samples drawn 0.5 m. under the arch.						
			Carbon dioxide.	Carbon monoxide.	Heavy hydrocarbons.	Marsh gas.	Hydrogen.	Oxygen.	Nitrogen.
June	A.M.								
	9.30	5 minutes after baiting the fire	4.2	0.2	0	0	0	15.1	80.5
	9.55		3.8	0.1	0	0	0	16.1	80.0
	P.M.		4.1	0.2	0	0	0	16.0	79.7
	12.20								409
	12.30	10 minutes after baiting the fire	3.3	0.2	0	0	0	16.4	80.1
	1.35		4.3	0.1	0	0	0	15.2	80.4
	3.50		3.4	0	0	0	0	16.8	79.8
	4.25	Immediately before firing	3.3	0.1	0	0	0	16.9	79.7
	4.50	20 minutes after baiting the fire	3.6	0.2	0	0	0	16.0	80.2
20	A.M.								
	9.30	Fire well established	15.0	0.2	0	0	0	3.1	81.7
	10.05	5 minutes after a heavy firing	16.1	0.6	0	0	0	0.9	82.4
	11.00	After the fire had burnt low	13.7	0	0	0	0	4.1	82.2
	11.45	Immediately after firing	15.0	2.0	0.3	0.5	0	0.2	82.0
	P.M.								
	4.35	Immediately after firing	16.2	0.1	0	0	0	1.8	81.9
	4.45	During the burning down of the fire	13.8	0.2	0	0	0	3.8	82.2
	5.15	Immediately before a new firing	7.9	0	0	0	0	12.0	80.1
	A.M.								
21	9.00	During the burning down of the fire	8.6	0	0	0	0	11.0	80.4
	9.40	10 minutes after firing	16.0	0	0	0	0	2.0	82.0
	11.30	20 minutes after firing	8.4	0	0	0	0	10.7	80.9
	P.M.								
	3.50	Before firing	7.0	0	0	0	0	13.1	79.9
	4.05	Just after firing	11.1	0	0	0	0	6.6	82.3
	5.10	During the burning down of fire	14.2	0	0	0	0	3.9	81.9
	6.00	Immediately after firing	11.9	0.3	0	0	0	5.8	82.0
	A.M.								
22	10.15	10 minutes after the firing	14.7	0	0	0	0	2.1	83.2
	10.30	During the burning down of fire	11.9	0	0	0	0	7.1	81.0
	P.M.								
	2.30	5 minutes after firing	16.5	0.9	0	1.1	0	0	81.5
	3.20	Immediately before firing	10.3	0	0	0	0	8.9	80.8
	3.45	After firing	11.9	0	0	0	0	6.2	81.9
	4.30	Burning off of the kiln	8.8	0	0	0	0	10.7	80.5

that the temperature in the kiln was too low to make complete combustion possible. With the increase of the heat the smoking of the chimney decreased; it appeared only immediately after fuel was supplied for a short time and in a slight degree. In spite of this the reducing gases in the fire gases could fre-

Xa

LOTTENBURG. BURN OF THE 19TH TO 22ND OF JUNE

Lower kiln.							Upper kiln.								
0.5 m. above the floor.							0.5 m. above the floor.								
Carbon dioxide.	Carbon monoxide.	Heavy hydrocarbons.	Marsh gas.	Hydrogen.	Oxygen.	Nitrogen.	Per cent of air.	Carbon dioxide.	Carbon monoxide.	Heavy hydrocarbons.	Marsh gas.	Hydrogen.	Oxygen.	Nitrogen.	Per cent of air.
4.2	0.3	0	0	0	15.6	79.9	391	3.8	0.2	0	0	0	15.9	80.1	394
3.8	0.2	0	0	0	16.2	79.8	422	3.7	0.2	0	0	0	16.2	79.9	421
3.8	0.2	0	0	0	16.4	79.6	445	4.0	0.2	0	0	0	16.2	79.6	426
3.6	0.2	0	0	0	16.2	80.0	418	3.4	0.1	0	0	0	16.4	80.1	435
4.4	0.1	0	0	0	15.2	80.3	348	3.9	0.1	0	0	0	15.6	80.4	371
4.5	0	0	0	0	15.9	79.6	402	3.5	0.1	0	0	0	16.4	80.0	437
3.5	0	0	0	0	16.8	79.7	483	2.9	0.2	0	0	0	17.3	79.6	519
3.7	0.1	0	0	0	16.2	80.0	418	2.9	0.1	0	0	0	17.1	79.9	499
16.0	0.1	0	0	0	2.1	81.9	111	14.0	0.2	0	0	0	3.8	82.0	120
15.9	1.3	0	0.4	0	0.2	82.2	93	13.6	1.1	0	0.2	0	2.7	82.4	108
15.6	0.6	0	0	0	1.9	81.9	108	14.4	0.6	0	0	0	2.8	82.2	113
15.3	2.0	0	0.2	0	0.6	81.9	96	15.6	1.4	0	0.2	0	0.4	82.4	97
16.1	0	0	0	0	1.9	82.0	109	14.2	0.2	0	0	0	3.6	82.0	119
15.3	0.1	0	0	0	1.9	82.7	109	9.1	0	0	0	0	10.7	80.2	200
9.3	0	0	0	0	10.1	80.6	191	7.8	0	0	0	0	12.0	80.2	228
8.9	0	0	0	0	10.9	80.2	205	4.0	0	0	0	0	14.8	80.2	322
15.8	0	0	0	0	2.2	82.0	111	15.0	0	0	0	0	2.8	82.2	115
12.1	0	0	0	0	6.2	81.7	140	11.5	0	0	0	0	7.5	81.0	153
7.8	0	0	0	0	12.4	79.8	240	8.1	0	0	0	0	11.6	80.3	219
15.9	0.9	0.1	0	0	0.5	82.6	99	11.7	0	0	0	0	6.2	82.1	139
14.0	0	0	0	0	4.2	81.8	124	8.7	0	0	0	0	10.1	81.2	186
15.4	1.9	0	1.4	0	0.3	81.0	83	15.1	0.1	0	0	0	3.0	81.8	116
15.4	0.2	0	0	0	1.8	82.6	108	12.0	0	0	0	0	6.3	81.7	141
13.6	0	0	0	0	4.6	81.8	127	14.7	0	0	0	0	3.0	82.3	116
16.4	0	0	0	0	1.0	82.6	105	15.8	0	0	0	0	1.8	82.4	109
10.2	0	0	0	0	8.9	80.9	171	10.0	0	0	0	0	9.2	80.8	175
14.1	0	0	0	0	3.2	82.7	117	13.5	0	0	0	0	4.4	82.1	122
7.0	0	0	0	0	12.9	80.1	253	10.4	0	0	0	0	9.0	80.6	173

TABLE II.  
TERRA COTTA KILN OF E. MARCH'S SONS, CHARLOTTENBURG. BURN OF THE 1ST TO 3RD OF AUGUST

		Aug. A.M.		Aug. P.M.		Sept. A.M.		Sept. P.M.		Oct. A.M.		Oct. P.M.	
		spikes drawn 0.5 m. under the arch.		0.5 m. above the floor.									
Lower kil.													
1		10.30 Second day of the burn; full fire; fires burning down when sample was taken		6.80.2 0 0 0 11.9 81.1221 7.30.1 0 0 0 11.1 81.5 203									
11.15		Before a new firing		6.40 0 0 0 13.2 80.4261 7.5 0 0 0 11.6 80.7 222									
11.20		At once after baiting; smoke scarcely visible		11.41.5 0 0.4 0 5.3 81.4.126 10.4.0.7 0 0 0 7.6 81.3 150									
P.M.		12.00 Fires well burnt down		13.91.40 0 10.2 0 2.3 82.1104 14.0.120.1 0 0 0 2.3 82.4 109									
3.00		Before a new firing		6.60 0 0 0 13.6 79.8278 6.9 0 0 0 13.2 79.9 264									
3.10		Immediately before a new firing; feeble white smoke		10.3 0 0 0 7.7 82.0154 12.20.3 0 0 0 5.4 82.1 133									
4.00		Fires burnt down low		10.7 0 0 0 8.4 80.9164 11.2 0 0 0 8.6 80.8 159									
5.00		Immediately after firing; feeble smoke		10.8 0 0 0 7.5 81.7152 11.6 0 0 0 6.9 81.5 146									
6.00		Immediately after firing; feeble smoke		14.00.1 0 0 0 3.5 82.4.118 14.40.1 0 0 0 3.4 82.1 118									
A.M.													
2		9.00 Immediately after firing		9.5 0 0 0 10.0 80.5188 10.8 0 0 0 8.4 80.8 164									
P.M.		12.30 Before firing; chimney without smoke		7.0 0 0 0 13.2 79.8264 8.1 0 0 0 12.0 79.9 201									
3.30		After firing		14.7 0 0 0 2.5 82.8116 14.8 0 0 0 2.5 82.7 113									
4.50		Before firing		10.6 0 0 0 9.2 80.2176 11.8 0 0 0 7.9 80.3 159									
5.00		After firing; dark smoke		14.52.5 0 0.70.1 1.7 80.6 95.15.51.5 0 0.2 0 2.2 81.4 105									
5.15		15 minutes later; the burn was finished the next morning		14.6 0 0 0 3.0 82.4.116 14.0 0 0 0 4.1 81.9 113									

quently not be discovered beside the large amounts of the oxygen present so that the appearance of light smoke cannot at once be interpreted as coincident with a reducing atmosphere. When the fire had burnt down, the excess of oxygen in the kiln had for the most part become so great that from two to two and one-half times the amount theoretically necessary was present.

According to the first series of experiments it seems as if the kiln atmosphere, on the whole, had been somewhat more reducing in the lower parts of the kiln, while from the average figures of the second burn a complete uniformity between the upper and lower kiln regions is noted.

*11. Porcelain Kiln of the Berlin Porcelain Co., formerly  
A. Schumann, in Moabit*

In its dimensions and general construction the kiln is similar to the previous one, but differs in the arrangement of its fireplaces. It possesses ten fireplaces distributed in pits around the kiln; in firing, these pits are partially covered with iron plates so as not to obstruct the passage around the kiln and the supply of fuel. The fireplaces are formed by flat grates about 0.5 meter wide and 0.75 meter long with deep ash pits; the openings for supplying the fuel, on a level with the ground, are covered with fire clay tiles. In the kiln there is in front of the fire openings, a low ring-shaped bench of fire-brick which spreads the flame and allows it to rise about 30 cm. above the kiln floor along the kiln wall from a ring-shaped slit. The flame rises to the arch, then descends and is drawn off in the bottom of the kiln, by a central flue and five radial flues arranged in a circle around it. The flame rises again in five flues, located in the kiln wall between the fireplaces, and enters the second story of the kiln which is used for the biscuit-burning of porcelain or for the burning of fire-brick and saggars. The total height of the kiln and chimney is about 15 meters; the time of the burn was about thirty-six hours.

The kiln was fired with a mixture composed of equal parts

of Bohemian lignite and lump coal, at intervals of about twenty minutes, with a vigorous draft. The samples were taken by means of porcelain tubes at three places, through one of the peep-holes immediately under the skew-back of the arch, in the door, at the middle between two fireplaces just within the flames coming from the furnaces on the way into the kiln and in one of the flues which conduct the flames of the lower kiln into the upper part likewise through one of the peep-holes.

Table XI contains the results obtained.

TABLE  
PORCELAIN KILN OF THE BERLIN PORCELAIN WORKS, FORMERLY

Day.	Hour.	Details and observations.	Samples drawn in the fire port.							
			Carbon dioxide.	Carbon monoxide.	Heavy hydrocarbons.	Methane gas.	Hydrogen.	Oxygen.	Nitrogen.	Per cent of air.
July 10	A.M.	The burn began at 6 in the evening of July 9th								
		10.00 Immediately after firing -	14.0	5.9	0.7	0.9	0	0	78.5	75
		10.10 Immediately after firing -	8.0	13.6	0.9	8.2	0	0	69.3	41
	P.M.	10.30 Immediately after firing -	14.2	5.7	-	-	-	-	-	-
		1.10 Fire burnt down low, just before a new baiting -	14.0	5.9	0	1.5	0	0	78.6	75
		2.00 Fires burnt down low, while cleaning grates of one of the fireplaces -	14.8	3.6	0	1.0	0	0.4	80.2	84
		2.30 Immediately after firing -	10.3	10.1	0	4.3	3.9	1.0	70.4	56
		3.50 Fires burnt down low, while cleaning the grates at a place beside where the sample was being taken -	15.0	0	0	0	0	4.2	80.8	123
		4.20 Immediately after firing -	10.8	10.6	0	2.8	0.2	0.2	75.4	64
		4.45 Immediately after firing -	10.9	10.3	0	2.8	0.1	0.1	75.8	65
		5.20 5 minutes after firing -	8.3	13.3	0	6.5	2.1	0.2	69.6	48
		5.55 Just after firing -	10.5	10.3	0	4.9	3.9	0.6	69.8	52
July 11	A.M.	11.00 15 minutes after the last fire	15.5	0.1	0	0	0	2.3	82.1	1111
		11.30	5.8	0.1	0	0	0	14.5	79.6	296
	P.M.	After the conclusion of the burn	4.7	0.1	0	0	0	15.6	79.6	374
			2.6	0	0	0	0	17.6	79.8	579

The results of the analyses of the second burn are not given here, because it was found that a part of the samples taken had not been enclosed perfectly air-tight by the loss of elasticity in a new kind of rubber tube used for closing the sample bottles.

We see also that the composition of the fire gases in the various parts of the kiln does not vary very much unless special circumstances which appear only from time to time during the burn, like the cleaning of the grates, explain the deviations.

## XI

## A. SCHUMANN, MOABIT. BURN OF THE 9TH TO 11TH OF JULY

Carbon dioxide.	Under the arches.							In the outlets.							
	Carbon monoxide.	Heavy hydrocarbons.	Marsh gas.	Hydrogen.	Oxygen.	Nitrogen.	Per cent of air.	Carbon dioxide.	Carbon monoxide.	Heavy hydrocarbons.	Marsh gas.	Hydrogen.	Oxygen.	Nitrogen.	Per cent of air.
17.7	0.1	0	0	0	0.9	81.3	104	16.9	2.0	0.20	0.2	0	0	80.7	91
12.8	7.0	0.3	2.9	0	0	77.0	66	13.5	6.3	0.72	1.1	0	0	77.4	68
14.7	2.4	—	—	—	1.8	—	—	11.1	7.0	0.92	0.0	0	0	79.0	67
16.0	0.4	0	0	0	1.9	81.7	109	16.4	0.4	0	0	0	1.3	81.9	105
11.2	0	0	0	0	8.5	80.3	166	13.5	0.1	0	0	0	5.1	81.3	131
11.2	6.8	0	2.6	2.2	0.4	76.8	68	11.2	10.6	0	4.1	3.6	0.5	70.0	54
10.0	11.2	0	3.2	1.4	0.2	74.0	61	11.0	9.1	0	2.0	0	0.9	77.0	72
13.1	3.3	0	1.6	0.1	3.1	78.8	91	14.3	4.8	0	2.4	0.5	1.0	77.0	75
15.0	4.0	0	1.1	0	0.3	80.6	84	14.2	5.8	0.4	1.4	0	0.1	78.1	75
10.1	10.0	0	3.8	1.5	0	74.6	59	10.3	10.9	0	3.1	3.5	0.1	72.1	58
12.0	7.1	0	2.7	3.1	1.3	73.8	67	14.5	4.6	0.1	2.4	0	1.5	76.9	77
12.8	6.9	0	0.6	0	0.5	79.2	83	14.0	5.0	0.20	0.8	0	0.3	79.7	82
7.2	0.1	0	0	0	13.0	79.7	259	7.3	0.1	0	0	0	12.7	79.9	248
4.2	0	0	0	0	15.9	79.7	401	4.5	0	0	0	0	16.0	79.5	412
3.5	0	0	0	0	16.8	79.7	483	2.8	0	0	0	0	16.7	79.5	476

The average values for the quantity of air supplied are :

	At the furnace mouth. Per cent.	Under the arch. Per cent.	At the exit. Per cent.
Immediately after firing -	57	63	71
Before supplying fresh fuel -	98	105	98

Immediately after firing, the condition for economical combustion is very unfavorable, since generally about a third, in a few cases even half, of the combustible gases remain unused, and even when the fire is completely burned down, before the charging of a new supply of fuel, there is present in most cases a considerable excess of combustible gases. We can, therefore, easily see that in some parts of the kiln no excess of oxygen could appear during the whole period of burning to consume the carbonaceous substances which are deposited especially at a low temperature, and this was evident from the character of the porcelain obtained. In many places of the kiln, and especially in thicker pieces, it had not become quite clear but was gray and opaque, a color effect which may well be referred to the influence of the fire gases before the fusing of the glaze, although when seen in incident light the porcelain appeared perfectly white and the glaze was free from defects.

A deposition of carbon in the pores of the porcelain mass, and perhaps also a reduction of metallic iron or carbide of iron at the high temperature of the porcelain fire, is not impossible, and may possibly be the cause of the gray color and the opacity of the porcelain. Direct experiments must give more definite information on this matter. That a reduction of the iron of the clay, with clays high in iron but at relatively low temperatures, can take place and become the cause of dark shades, has already been proved experimentally,<sup>1</sup> and would explain many phenomena in connection with porcelain and appearing in burning if it could be proved for the higher temperatures and under the

<sup>1</sup> *Thon-Industrie Zeitung* 1877, p. 8.

conditions existing in the kiln. Such a reaction, however, could only be expected under the supposition of an excess of reducing gases beyond a certain point, and this agrees with the phenomenon that a gray or brown coloring of the porcelain—of the body or the glaze—does not invariably develop in a reducing and sooty kiln atmosphere which is nearly always present in a porcelain kiln, as we see from the analyses. We might think of the reaction of iron and its oxides, which must be considered for the explanation not only of the present, but also of other phenomena. In a current of hydrogen (also hydrocarbons), the oxides of iron are changed into metallic, spongy iron when brought to a red heat, while at the same time water vapor is formed. On the other hand metallic iron in a current of water vapor changes to the ferroso-ferric oxide, at the same time evolving hydrogen. With the same agents we have here, therefore, opposite reactions, the only difference being that at one time the iron or its oxygen compound is in an atmosphere in which the hydrogen is in excess and at another time the water vapor is in excess. Chemistry knows many examples of such phenomena in which the active agent and the product can bring about opposite reactions, according as one or the other is quantitatively in excess. The substances here in question are always present in the operations in the kilns of the ceramic industry, iron in the clay, hydrogen (or hydrocarbon) and water vapor in the fire gases. It will, therefore, always depend on the mutual relation of the latter, which of the opposite reactions can take place by the excess of one or the other. It follows from this that the action or influence of the agents of the fire gases on the iron compounds and the phenomena connected with them, can take place all the more easily, that is, with a smaller amount of fire gas the poorer it is in water vapor and vice versa. A large amount of water vapor in the fire gas will be able to prevent a reduction of iron compounds to the black coloring, opaque metallic iron and permit only compounds corresponding to the lower stages of oxidation, which are soluble in melting silicates and form transparent masses.

This is, perhaps, one of the explanations for the phenomenon affirmed by practice in all branches of the clay industries, that with the use of fuels high in hydrogen (therefore forming much water vapor on burning), such as wood, peat, lignite, the phenomena referred to "smoking" appear less frequently than when coal less rich in hydrogen is used in burning.

#### *12. Gas Kiln of the Royal Porcelain Factory*

The kiln<sup>1</sup> is a continuous one which consists of 22 chambers, 2.75 m. long, 2.45 m. wide, and 2.20 m. high, arranged in two rows of eleven each. Each of these chambers communicates with a common smoke flue lying parallel between the two lines of chambers, and through it with a high chimney by means of a flue that can be closed by an iron valve. Each of the chambers possesses, on one of its long sides, a fire bridge, 1.20 m. high with a space of 0.12 m. between it and the kiln wall which is braced at its middle against the latter. On the opposite kiln wall there are distributed at the level of the kiln floor eight vents for the escape of the flames, which open into a cross flue under the floor. From this transverse flue the flames can pass through two short wide flues, arranged in the axis of the kiln beneath the partition wall of the chambers to the next chamber, and enter behind its fire bridge. In the same way as the chambers of a row, the end chambers of the two rows are connected by means of flues so that the flame passing from one chamber series can be led into the other. In this manner communication is established for the movement of the air supporting the combustion and for the flames passing away from chamber to chamber, which, however, can be cut off behind each chamber by the insertion of a fire-clay tile.

The gas used for combustion is produced in two shaft generators, passes from these into a common flue which splits into two branches that pass along each series of chambers; from these

<sup>1</sup> For a description and drawing see G. Moeller, "The New Plant of the Royal Porcelain Factory," 1872, Berlin, published by Ernst and Korn.

a branch, which may be closed by means of an iron valve, passes under the kiln floor of every chamber. The gas passes from two openings of the gas main into the air flues connecting the chambers, mixes with air behind the fire bridge, and enters the kiln ignited behind the bridge, spreading out fan-like close to the arch of the kiln. The air serving to feed the fire enters through one of the open doors of the kiln and first passes through three or four chambers that are cooling, always passing up and down over the fire bridges until it gets to the one which is at full fire. In this manner the air is highly preheated. The heat passing off likewise passes through three or four of the next chambers which are thus heated, and then through the smoke flue, open in the last one, into the chimney. When the ware in one chamber is burned, which requires a period of firing of from ten to fifteen hours, the corresponding gas flue, leading to it, is cut off and the gas allowed to pass into the next chamber which has already been heated to beginning white heat, so that the gas ignites at once. At the same time the outlet vent is opened one chamber ahead and the one last used is closed. In this cycle, which the fire thus describes, the ware is burned to the glost heat in the one row and to the biscuit heat in the other. The last chamber is filled with fire-bricks or saggers in order to lessen the abrupt change in temperature.

To obtain the samples of fire gases porcelain tubes were introduced into the kiln in the door, under the door arch which is 1.60 meters high, and 0.2 meter above the kiln floor to the length of 1 meter; the tubes were protected against bending by being supported by saggers cut to fit the tubes. In part the gas was taken by means of a fire-clay tube bent at right angles immediately at the kiln arch.

The samples were taken from one biscuit burn, two glost burns for white, and three glost burns for porcelain decorated in blue. The tables XII $\alpha$  to  $f$  contain the results obtained.

TABLE XIII.—*GAS KILN OF THE ROYAL PORCELAIN FACTORY.* Biscuit Burn on 4th June, 1878

TABLE XIII.—GAS KILN OF THE ROYAL PORCELAIN FACTORY. Biscuit and Glosburn on 27th and 28th May

Date	A.M.	9-30 Firing in chamber 1, tests in chamber 3, therefore the 2nd chamber is being heated up		P.M.
		10.30	11.30	
27	10.30	14.2 0.7 17.5 0.3 16.9 0.1	0 0 0	0 0 0
	11.30	0 0 0	0 0 0	0 0 0
	P.M.	0 0 0	0 0 0	0 0 0
	12.30	0 0 0	0 0 0	0 0 0
	1.30	0 0 0	0 0 0	0 0 0
	2.30	0 0 0	0 0 0	0 0 0
	A.M.	- - -	- - -	- - -
	3-30	Firing in chamber 2, tests in chamber 3, therefore the first chamber is heating up	- - -	- - -
4-30	10.30	15.9 1.6 15.9 2.2 15.7 3.1 15.7 3.1 13.8 0	0 0 0 0 0	0 0 0 0 0
5-30	11.30	0 0 0 0 0	0 0 0 0 0	0 0 0 0 0
6-30	P.M.	0 0 0 0 0	0 0 0 0 0	0 0 0 0 0
	12.30	0 0 0 0 0	0 0 0 0 0	0 0 0 0 0
	1.30	0 0 0 0 0	0 0 0 0 0	0 0 0 0 0
	2.30	0 0 0 0 0	0 0 0 0 0	0 0 0 0 0
	3-30	On conclusion of burn the admission of gas charged to chamber 4 12.3 0.3	0 0 0 0 0	0 0 0 0 0
	A.M.	- - -	- - -	- - -
	4-30	9-30 Firing and test in chamber 3, therefore on high fire	- - -	- - -
5-30	10.30	12.9 0 13.1 0.4 12.8 0.1 12.5 0.8 14.6 0.9	0 0 0 0 0	0 0 0 0 0
6-30	11.30	0 0 0 0 0	0 0 0 0 0	0 0 0 0 0
	P.M.	0 0 0 0 0	0 0 0 0 0	0 0 0 0 0
	12.30	0 0 0 0 0	0 0 0 0 0	0 0 0 0 0
	1.30	0 0 0 0 0	0 0 0 0 0	0 0 0 0 0
	2.30	0 0 0 0 0	0 0 0 0 0	0 0 0 0 0
	3-30	0 0 0 0 0	0 0 0 0 0	0 0 0 0 0
	4-30	On conclusion of burn the admission of gas charged to chamber 4 12.3 0.3	0 0 0 0 0	0 0 0 0 0

Contents of the kiln was porcelain exclusively. The result of the burn was free from defects.

TABLE XIIc.—GAS KILN OF THE ROYAL PORCELAIN FACTORY. Glost-burn on 31st May

May	A.M.	10.00 Tests taken from chamber 8 in high fire	-	-	14.1 4.3 0.5 0.7	0	0	80.4	81.12 6.5 9.0 9.9	0.9	0	0.279.5 7.9
31	11.00				15.6 2.8 0.6	0	0	0.280.8	88.14.1 0.1	0	0	3.382.1112
	12.00				14.5 4.1 0.9	0	0	0.280.3	82.14.8 0.2	0	0	3.082.0116
	P.M.											
1.00		Admission of gas changed to chamber 9	-	-	14.7 4.0 5.0 1.0	0	0	0.081.3	92.16.4 0.2	0	0	1.182.3105
2.00		Admission of gas changed to chamber 9	-	-	13.8 5.0 0.9 0.4	0	0	0.475.5	7916.1 0	0	0	2.081.9110

Content of the kiln was porcelain exclusively. Result of burn free from defects.

TABLE XIIa.—GAS KILN OF THE ROYAL PORCELAIN FACTORY. Glost-burn for blue painted porcelain 31st May

May	P.M.	3.00 Gas inlets and tests in chamber 9. The pottery painted blues	5.2	2.8 0.5	0.2	0	0	81.3	87			
31	4.00	under the glaze begins only in the upper portion of the kiln	12.2	8.8	0	1.3	1.0	0.4	76.3	74		
	5.00	0.6 meter above the floor of the kiln, and in the back portion	12.6	7.8	0	1.0	1.6	0.3	76.7	70		
	6.00	of the kiln a second perforated fire-wall is placed through	13.8	6.6	0	1.2	0.3	0	78.1	76		
	7.00	which the flames were drawn out to chamber 10	13.4	6.6	0	1.4	0.6	0.1	77.9	77		

Porcelain was a good white, blue decoration was strongly bubbled up and gray.

TABLE XIIe.—GAS KILN OF THE ROYAL PORCELAIN FACTORY. Glost-burn for blue painted ware on 25th June

Porcelain a good white, blue decoration only a little bubbled and pure blue.

TABLE XII

July	A.M.	1.6 m. above the kiln floor.									
		10.15	11.15	12.00	1.0	1.0	1.0	1.0	1.0	1.0	1.0
4		Fire and tests in chamber 9, contents and setting as above	-	-	12.2 10.5	0.2	0	0	0	7.881.5155	
		End of the burn	-	-	10.5 12.0	0	0	0	0	6.681.4144	

Porcelain good white, blue decoration pure blue and free from bubbles except a few pieces in the uppermost ~~uppermost~~ <sup>uppermost</sup> pieces immediately at the fire bag.

In the biscuit burn examined, there was always a considerable excess of air which, in the most cases, is somewhat larger at the floor of the kiln than under the arch and the middle, exceeding the theoretically necessary amount in the lower part by 74 per cent, and by 46 per cent in the upper part. The same phenomenon of excess of atmospheric air in the lower parts of the kiln is also found in most cases in the glost-burn. Table XIIb gives a complete representation of the course of the glost burn from a just visible red heat to the highest temperature. There appears in the first stages of the burn a great uniformity in the composition of the fire gases; at any rate the deviations are much smaller than with all the kilns which are fired directly, with the single exception of the one fired with wood as fuel and using an inclined grate.

The average figures for the percentage of air used in the burns for white porcelain show:

	Under the arch. Per cent.	At the kiln floor. Per cent.
<b>From Table XIIb in the glost burn :</b>		
a. Two chambers before the fire -	102	120
b. One chamber before the fire -	88	91
c. In the full fire -	123	86
From Table XIIc in the full fire -	85	104

The excess of air in the lower parts of the kiln during the low heat may perhaps be explained by the fact that the kiln walls allow air from the outside to pass through, which can never be avoided, on account of the lower pressure which the fire gases possess as compared with the external atmosphere, and that this air from without, on account of its lower temperature, chiefly is found in the lower part of the kiln. It may well be assumed that even if the fire gases in the division which is in full fire do not show an altogether homogeneous composition at the various heights, still the differences must vanish by the double passage through the narrow connecting flues between the kiln chambers. That a further mixture takes place is clear when we compare

the figures which were obtained in the case of the low fire and the full fire. While the latter, especially in the upper parts of the kiln, show considerable amounts of oxygen beside combustible gases, the oxygen disappears more and more in the chambers at a low heat.

In the full fire there is an excess of combustible gases, or as the case may be, a smaller amount of oxygen, at times in the upper parts of the kiln and sometimes in the lower. In the majority of instances the former is the case, but also in the same series of experiments a change is observed. It is seen from this that during a longer time of burning an excess of air may constantly be present in a certain part of the kiln without producing any noteworthy injurious effect.

As was the case with the vertical porcelain kiln discussed before, there appears also here the phenomenon that the underglaze decorations of cobalt oxide come out of the burn the more perfect the less reducing was the kiln atmosphere, at least in the last stages of the burn.

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The conclusions which may be drawn from the preceding analyses of the fire gases are, in short, as follows:

1. If reducing gases appear in the fire gases, be it through a deficient supply of air, or on account of an insufficient mixing of the air with the distillation products of the fuel, they are, as a rule, the richer in hydrogen the greater their amount, and become the richer in carbon the smaller their quantity. The hydrocarbons may therefore be looked upon, in the first case, as being chiefly a mixture of marsh gas and hydrogen, in the latter as ethylene and marsh gas.

2. With a decrease of the reducing constituents in the fire gases, hydrogen and the hydrocarbons vanish first, while carbon monoxide is, as a rule, still present in considerable amounts when the former can no longer be found. In many cases carbon monoxide is found even when oxygen is already present in excess, especially when the temperature of the kiln is low.

3. The appearance of smoke or soot is a probable, but just as little an absolutely certain, indication of an excess of reducing gases in the fire gases as its absence indicates an excess of oxygen. In spite of a decidedly oxidizing character of the fire gases, smoke appears all the more easily and persistently the lower the temperature of the kiln; frequently, however, especially at high temperatures, the smoke has disappeared while the fire gases still contain considerable amounts of combustible gases.

4. The order in which the volatile combustible compounds burn on their way through the kiln, seems to be the following: Hydrogen, marsh gas, ethylene, carbon monoxide, soot. In many cases, especially when the temperature was low, the simultaneous presence of oxygen and combustible gases in the fire gases could be observed.

5. The differences appearing in the composition of the fire gases depend not only on the construction of the fireplaces, the amount and kind of fuel, and the intervals in which it is supplied, but also on the direction of the fire gases in the kiln.

6. With a uniform supply of fuel (inclined grate firing) or with a periodic supply of preheated or ignited fuel (step grate), no considerable deviations in the composition of the fire gases appear in successive intervals unless the conditions of the combustion are changed. With the periodic supply, on the other hand, of cold fuel, considerable differences appear which at one time bring about a great excess of reducing gases, and again an excess of atmospheric air even to ten times the amount theoretically necessary.

7. In kilns in which the flames pass up vertically, or up and down, for the most part no great differences in the composition of the fire gases appear at various heights; if any such differences appear in kilns in which the flames rise perpendicularly the lower parts are higher in reducing gases or, as the case may be, poorer in free oxygen. With down-draft kilns the gases are sometimes more reducing in the lower, sometimes in the upper, parts. In kilns where the flame has a hori-

zontal direction there is constantly a great excess of atmospheric air in the upper or, as the case may be, the front parts of the kiln, in such a way that in the upper parts an oxidizing atmosphere prevails, and at the same time a reducing condition in the lower parts. An equalization takes place only when the fire is burnt down very low; very strong firing causes reducing gases in the upper parts of the kiln, but only in small amounts and for a short time.

8. At the conclusion of the burn a vigorous oxidizing effect of the kiln atmosphere appears at all times. When the fire-places are closed air-tight at the close of the burn, the amount of oxygen decreases in a noticeable manner when there are still some coals left, so that under these circumstances a temporary or local appearance of carbon monoxide may be expected during the period of cooling.

9. In those branches of industry which use relatively low temperatures up to beginning white heat (brick, terra cotta, ordinary faience ware), the character of the kiln gases is mostly strongly oxidizing. The fluctuations, when the carbon compounds are on the increase, for the most part, go only to the limit of the neutral condition, or cause a temporary weak reduction. Only with the kilns that have a horizontal direction of draft is the reducing effect very vigorous, but usually only in the lower parts.

10. In those branches of the industry that use higher temperatures the character of the flame is strongly reducing, partly during the entire burn, partly only during a period of the same. In general the fluctuations vary from a point at which only one-half or two-thirds of the combustible gases can be consumed up to a neutral condition of the flame or to a weakly oxidizing effect. Frequently also the reducing effect predominates during long periods.

11. To the content of ferric oxide in the impure and porous clays, a noteworthy cooperation must be ascribed in the combustion, as an aid to the atmospheric oxygen, in such away that it

gives off a part of its oxygen in a reducing atmosphere only to take it up again during a subsequent oxidizing period.

12. In clays containing lime a volatilization of sulphur compounds coming from the clay or the fuel takes place only in a reducing, but not in an oxidizing, atmosphere; when the reducing gases are slightly in excess the sulphur appears in the form of sulphurous acid, with a great excess in the form of hydrogen sulphide.

13. On the white enamel glazes, containing tin and lead, a reducing atmosphere exerts no harmful influence if the reducing atmosphere is followed by a sufficiently vigorous oxidizing condition continuing for some time; it even seems as though an alternately reducing but finally oxidizing effect has a favorable influence in regard to a pure white color and prevents the appearance of reddish shades.

14. In the burning of porcelain the kiln atmosphere, as a rule, exerts a reducing effect on the body; a temporary moderate excess of reducing gases seems to be favorable to the production of a white or bluish color; but an excess of air, even continued for long periods, seems to produce no injury.

15. In the case of porcelain with blue underglaze colors, the bubbling appears the stronger and the blue color the less bright, the more reducing the kiln atmosphere, especially during the last stages of the burn.

### The Temperature and Composition of Fire Gases in Some Continuous Kilns

PROFESSOR CHAS. W. MESLOH, TRANSLATOR.

Mr. Ferd. Fischer,<sup>1</sup> in Hannover, has recently published an essay in Dingler's *Polytechnisches Journal*, concerning the burning of bricks in continuous kilns, in which he gives the meas-

<sup>1</sup> Dr. F. Fischer, "Concerning the Burning of Bricks in Continuous Kilns," Dingler's poly. J., 228, 432 (1878).

urement of temperatures and analyses of fire gases that were made in two continuous kilns containing fourteen chambers each in the vicinity of Hannover, at Stöcken and at Linden Berg. The measurements of temperature which extended to all parts of the kiln, were measured for the lower temperatures up to 300° C., by means of suitably constructed mercury thermometers, and the higher temperatures by means of an electrical pyrometer made by the Siemens Brothers, in London, which has been repeatedly described in the ceramic periodicals. According to the observations made, the highest temperature observed in the kiln near Stöcken was 1057° C., while the gases in the chimney escaped at 108° to 172° C. In the kiln at Linden the highest temperature was almost 100° lower, namely, 968° C., while the temperature of the escaping kiln gases went down to 80° C. The results of the measurements which the author represents graphically in two diagrams are given in the following table in which the figures in the vertical columns indicate the temperatures at the front and at the end of the separate kiln chambers:

Continuous kiln at Stöcken.			Continuous kiln at Linden Berg.		
	No. of chamber.	Temperature.		No. of chamber.	Temperature.
Water smoking.	8	80-130° C.	Water smoking.	10	60-80° C.
	7	130-219° "		9	80-200° "
	6	210-400° "		8	200-440° "
	5	400-700° "		½ 7	440-660° "
Being fired.	4	700-880° "	Being fired.	½ 7	660-800° "
	3	880-1057° "		6	800-960° "
				5	960°
				½ 4	960-800° "
Cooling.	2	1000-600° "	Cooling.	½ 4	800-660° "
	1	600-360° "		3	660-490° "
	14	360-160° "		2	490-300° "
	13	160-80° "		1	300-120° "
Being emptied and set: 12, 11, 10, 9.			Being emptied and set: 13, 12, 11.		

Especially interesting in these observations is the circumstance that in the kiln in Stöcken, finishing a cycle burn in seven to eight days, the temperature rises steadily up to its greatest heat, and from this point on falls just as constantly, while with the slower kiln at Linden, which completes a burn in fourteen days, with a more gradual increase and decrease, the

#### I. CONTINUOUS KILN AT STOCKEN, 24TH JULY, 1877

Under the arch.					At the kiln floor.				
Time of the observation.	Carbon dioxide.	Carbon monoxide.	Oxygen.	Nitrogen.	Time of the observation.	Carbon dioxide.	Carbon monoxide.	Oxygen.	Nitrogen.
A.M.					A.M.				
9.45	4.1	0.0	16.6	79.3	10.00	7.5	0.0	12.9	79.6
10.10	4.4	0.0	16.4	79.2	11.00	9.1	0.0	11.4	79.5
11.05	5.1	0.0	15.6	79.3	11.10	11.7*	0.0	8.7	79.6
11.18	6.0	0.0	14.6	79.4	11.28	11.1*	0.0	9.3	79.6
11.37	5.2	0.0	15.6	79.2	11.45	9.6	0.0	10.9	79.5
P.M.					P.M.				
12.00	5.8	0.0	14.8	79.4					
1.50	1.1	0.0	19.9	79.0	1.59	1.3	0.0	19.6	79.1
2.15	3.0	0.0	17.9	79.1	2.30	7.8	0.0	12.9	79.3
2.36	3.4	0.0	17.6	79.0	2.45	7.7	0.0	12.6	79.7
2.48	3.4	0.0	17.3	79.3	3.03	7.5	0.0	13.0	79.5
					3.12	8.3	0.0	12.3	79.4
3.17	3.0	0.0	17.9	79.1	3.22	7.8	0.0	12.8	79.4
3.28	3.2	0.0	17.6	79.2	3.33	10.0*	0.0	10.2	79.8
3.39	3.8	0.0	17.0	79.2					
3.50	4.8	0.0	15.9	79.3	3.57	11.8	0.0	8.4	79.8
4.03	5.4	0.0	15.2	79.4	4.12	11.8	0.0	8.2	80.00
4.17	5.8	0.0	14.9	79.3	4.23	11.2	0.0	9.2	79.6
4.28	6.2	0.0	14.5	79.3					
4.37	3.2	0.0	17.7	79.1	4.45	12.2	0.0	8.0	79.8
4.52	6.0	0.0	14.8	79.2	4.50	9.8	0.0	10.6	79.6
5.05	4.8	0.0	16.1	79.1	5.15	14.2*	0.5	5.8	79.5
5.24	5.0	0.0	15.8	79.2	5.31	10.2	0.0	10.1	79.7
					5.40	11.2	0.0	9.1	79.7

highest temperature is maintained uniformly in a larger part of the kiln, and therefore insures a greater uniformity in the burn.

According to the measurements obtained, the clays burned in the kilns in question must be classified with the easily fusible ones. Peclet's statement that the temperature of brick kilns is to be taken at from 600° to 700° C., is hence taken too low; it seems to be nearer the melting-point of silver, 960° C.

## II. CONTINUOUS KILN AT LINDEN, 24TH SEPTEMBER, 1877

Under the arch.					On the kiln floor.				
Time of observation.	Carbon dioxide.	Carbon monoxide.	Oxygen.	Nitrogen.	Time of observation.	Carbon dioxide.	Carbon monoxide.	Oxygen.	Nitrogen.
A.M.					A.M.				
10.02	2.3	0.0	18.7	79.0	10.10	7.3	0.0	13.8	78.9
10.20	2.1	0.0	18.9	79.0	10.25	4.8	0.0	16.1	79.1
					10.35	5.4	0.0	15.4	79.2
10.44	2.4	0.0	18.6	79.0					
10.55	2.6	0.0	18.3	79.1	11.01	7.0*	0.0	13.8	79.2
					11.35	10.7	0.0	10.0	79.3
11.42	5.6	0.0	15.3	79.1	11.48	7.6	0.0	13.5	78.9
11.54	4.5	0.0	16.4	79.1	12.00	7.6	0.0	13.2	79.2
P.M.					P.M.				
12.06	5.5	0.0	15.5	79.0	12.12	7.0	0.0	13.9	79.1
12.17	7.9*	0.0	13.2	78.9	12.24	8.2	0.0	12.7	79.1
12.30	4.7	0.0	16.2	79.1					
12.39	4.3	0.0	16.7	79.0	12.45	18.4*	0.0	2.2	79.4
12.51	5.0	0.0	16.0	79.0	12.59	6.2	0.0	14.6	79.2
					1.05	9.4*	0.0	11.5	79.1
1.13	4.2	0.0	16.9	78.9	1.19	6.8	0.0	14.4	78.8
					1.26	8.5	0.0	12.4	79.1
1.32	4.8	0.0	16.3	78.9	1.40	6.7	0.0	14.3	79.0
					1.46	6.2*	0.0	14.7	79.1
					1.52	10.6	0.0	10.2	79.2
					2.00	8.4	0.0	12.5	79.1
2.14	7.7	0.0	13.3	79.0	2.20	10.1*	3.8	8.1	78.0
2.46	3.2	0.0	17.8	79.0					
2.56	3.1	0.0	17.7	79.0					

In connection with the determination of temperature in the kilns named there were taken analyses of the fire gases; these gases were drawn from the kilns 0.30 meter below the crown of the arch and at the floor of the kiln. In general the samples were taken alternately above and below, those immediately following being placed side by side in the table; those designated with an asterisk were taken immediately after coal had been supplied.

In considering Tables I and II we first notice that the amount of unused air passing through the continuous kiln is far greater in the upper part than at the floor, and therefore the generation of heat must be greater near the kiln floor. If we take the average figures from these tables they are found to indicate that in the upper part of the twenty-one parts by volume of oxygen which enter the kiln with 100 parts of fresh atmospheric air, only 4.3 parts (in both kilns) are used for the combustion of coal to carbon dioxide below the crown, and 8.4 (Stöcken) and 8.2 (Linden) at the floor of the kiln; that is, approximately only one-fifth of the oxygen was used under the crown, and two-fifths near the floor. Such a combustion would be called very uneconomical in a kiln that is not continuous, still such conditions are found probably in hundreds of continuous kilns, and may be considered the rule. Nevertheless, if the continuous kilns do far exceed most other kilns in fuel economy it is because the heat once generated is used again and again for new work, the heat of the discharged gases is used for water-smoking, and that of the cooling bricks for preheating the fire gases up to almost the maximum temperature; thus, the losses caused by the great excess of air are more than compensated for. The tables also show that, as a rule, we cannot assume the evolution of combustible gases, because of insufficient oxygen in the presence of so great an excess of air, and in fact carbon monoxide appeared, only in a few cases, in small amounts, immediately after firing, and always in the presence of an amount of oxygen more than sufficient for its combustion, so that its presence must be ascribed to incomplete combustion. That, how-

ever, a temporary appearance of unburnt gases, with the simultaneous absence of oxygen, is absolutely necessary for the development of many, especially light, colors has been repeatedly stated; on the other hand the relatively rare appearance of reducing gases, that is, unconsumed decomposition products of coal, explains also the difficulties which have been met in the production of pure colored face brick in the continuous kiln with its relatively large excess of air. Knowing the causes which are the basis of this poor success of the continuous kiln as compared with the old, wasteful kilns, the fault is easily remedied.

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### Composition and Specific Gravity of Generator Gas

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PROF. CHAS. W. MESLOH, TRANSLATOR

Technologists are at present striving to extend the use of gas firing, and in spite of many failures its great importance for the future cannot be denied. In view of the great literary activity in this field, it seems strange that so very little positive material has been published concerning the composition of generator gases; even in the latest works the calculations made on the efficiency of gas firing rest almost exclusively on the hypothetical composition of generator gases according to the composition of the coal and not on that which actually results in practice and which must vary considerably according to the more or less perfect construction of the generators. Still it seems of great practical importance to know the composition of the gaseous fuels derived from the solid fuels, especially when comparing the value of different generating systems and determining their efficiency in the use of different fuels. The following analyses may therefore serve as a contribution to a better understanding on this point.

The generator gases investigated were taken from the gas-

pipe connecting the generators and the gas kiln of the Royal Porcelain Factory in Berlin.

The samples were taken on the 29th of May, at intervals of one hour; fifteen minutes were consumed in the operation so that the gas represents the average of one-fourth of the time. Two generators were in operation, charged alternately in intervals of one hour; the time of charging falls about in the middle between that of the separate observations. The generators are rectangular shaft generators<sup>1</sup> with plain bar grates and were fed with coal, half English and half Upper Silesian.

The analyses gave the following results in percentages by volume:

Number of the test.	Time of drawing the sample.	Carbon dioxide.	Carbon monoxide.	Marsh gas. <sup>2</sup>	Hydrogen.	Oxygen.	Nitrogen.	Calculated specific gravity.
	A.M.							
1	9.30	4.2	23.7	6.8	3.3	0.1	61.9	0.9359
2	10.30	4.6	21.5	7.0	2.4	0.5	64.0	0.9460
3	11.30	3.7	23.7	6.7	2.2	0.2	63.5	0.9436
	P.M.							
4	12.30	1.9	23.4	6.8	1.4	1.8	64.7	0.9425
5	1.30	3.3	23.3	7.0	1.4	0.5	64.5	0.9477
6	2.30	3.9	23.4	7.0	2.3	0.1	63.3	0.9424
7	3.30	2.9	23.1	8.1	2.6	0.4	63.5	0.9455
8	3.45 <sup>3</sup>	3.4	22.7	9.3	3.3	0.2	61.1	0.9211
9	5.30	4.5	21.8	7.0	1.4	0.3	65.0	0.9542
	Average	3.6	22.8	7.4	2.2	0.5	63.5	0.9421

The specific gravity of the gas has been calculated from the preceding analyses; it must, however, be noted that no attention was paid to the amount of tar and water in the gas. The refer-

<sup>1</sup> Concerning the details of the construction and the measurements see G. Moeller, "The New Plant of the Royal Porcelain Factory, 1873," published by Ernst & Korn in Berlin.

<sup>2</sup> The hydrocarbons contained in the gas are calculated as marsh gas, because the product of dry distillation is chiefly marsh gas.

<sup>3</sup> The sample was taken while one of the generators was being cleaned.

ence to the specific gravity was only to call attention to a point heretofore not sufficiently noted, namely, that the specific gravity of gas, when as in this case fuel low in water content is used, does not vary very much from that of atmospheric air at the same temperature, and that the temperature at which air and gas enter the kiln will essentially determine how these will move through it in separate currents. According to the calculation taken as a basis, the slight temperature difference of 16° C. would suffice to equalize the difference of the specific gravities of air and gas. The resistance to the intimate mixture of gas and air in the kiln due to the difference in specific gravity will be the less the smaller the difference of temperature is between the gas and air and the tendency to form zones of different composition will be the greater the greater this difference is. If we assume that generator gases enter the kiln at 200° C., if the gas main is not too long, then in such kilns in which the gas is burnt with cold air, the gas will be the lighter constituent and tend to take the upper parts of the kiln; in the case of continuous kilns, on the other hand, in which the air for combustion has usually a very high temperature, up to 1000° C., the reverse must take place, and the gas will then tend to occupy the lower parts of the kiln.

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### An Explanation of the Action of "Water" in the Burning of Clay Ware

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PROF. CHAS. W. MESLOH, TRANSLATOR

A long series of phenomena which appear in the burning of clay ware and may cause serious losses, are ascribed by practical men to the influence of water vapor; but in most cases it has not been possible to explain how the phenomena occur. Troubles such as cracks, discolored, scaly or mealy coatings and motley colors on the body, scaling and dimming of the glaze, vanishing of individual colors, etc., undoubtedly are in some

way influenced by water vapors that pass through the kiln, as practical observations have shown, since they become much more pronounced when an increased formation of vapor takes place, due to the setting of wet ware, kiln repairs, damp fuel, etc. Although this connection is undoubted, it seems inexplicable in what way the phenomena mentioned are brought about, on account of the stability of water vapor and its indifference to silicates; the following investigation will throw light upon at least a few points.

Clay, or the body prepared from it, is a very hygroscopic substance, which when completely dried will draw moisture from the atmospheric air with great avidity and retain it in its pores. If we place clay, perfectly dried at a higher temperature, under a glass bell, together with a vessel filled with water, it will feel clammy after a few days, and if we determine its weight as well as that of the water with an accurate balance we will find that the former has increased considerably in weight and the latter has diminished just as much. These hygroscopic qualities of clay in general appear all the more pronounced the more unctuous it is, and the amount of water taken up in a few days at ordinary temperature is frequently over 10 per cent of the weight of the clay. Water is taken up all the more rapidly and energetically, the richer the air in contact with the clay is in water vapor. At a higher temperature, where the capacity of the air of absorbing water vapor increases very rapidly, the absorption of water by the clay will also be more rapid than at ordinary temperatures. From this it becomes clear that newly set clay wares must nearly always take considerable amounts of water from the fire gases during the first stages of the burning, and it is well known that this absorption of water sometimes leads to a softening,—to a greater or less change in shape. The amount of moisture in the air surrounding the clay wares in the kiln, depends on circumstances which are chiefly of accidental nature, the condition of the ware as regards dryness, the intensity of the draft, the more or less dry condition of the kiln, the character

of the fuel, etc. In most cases, however, it is very considerable so that even at rather high temperatures injurious effects may be attributed to condensation on a large scale. A few determinations which were made under very favorable conditions (inasmuch as only the water of the fuel could be looked upon as the cause of the vapor formation), will make this clear. They refer to the determination of the aqueous vapor present during the glost-burn in the porcelain kilns of the Royal Porcelain Factory, which showed 17.88 and 15.37 per cent by volume of water vapor in two determinations, during the glost-burn in a small, round, two-story test kiln for porcelain, 1.60 meters wide and 1.75 meters high, using dry wood as a fuel and firing on inclined grate furnaces, and 9.72 and 7.75 per cent by volume in the glost-burn of the gas kiln at the porcelain factory.<sup>1</sup>

According to this the dew point of the fire gases would be calculated in the first case to be 58.5° and 55.5° C., respectively, and in the latter case 46.5° and 42.0° C., respectively, that is, the fire gases are so charged with water vapor that when they are cooled below the temperatures given, even without considering the water-absorbing property of clay with which they might come in contact, water would be deposited on the surface of the ware in globules.

If we assume this condensed liquid in the pores and on the surface of clay wares to be chemically pure water which would have to be evaporated again at a higher temperature, and would not leave any residue, we could not explain through it other phenomena excepting those which are connected with the softening of the clay. These condensations, however, by no means consist of pure water and the phenomena ascribed to the water are not to be charged to it, but to the substances accompanying it. By entering the pores or by condensation on the surface, water brings about the absorption of the injurious substances

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<sup>1</sup> Illustrated and described by G. Moeller: "The New Plant of the Royal Porcelain Factory at Berlin, Berlin, 1873," published by Ernst and Korn.

and is, therefore, only indirectly the cause of the phenomena generally ascribed to it.

In order to know the nature of the substances accompanying the water vapor, the source of which we assume to be partly the body of the clay ware itself, and partly the fuel or its ashes, the attempt was made to condense considerable amounts of moisture from the fire gases in the kilns above mentioned. The examination of these precipitates is interesting in so far as they represent in a measure the lower limit of possible impurities, since the relatively purest fuels were used, such as wood and generator gas made from pure coal; with more impure fuels the amounts of impurities would probably have been considerably higher, which coincides with practical experience.

The condensable constituents of the fire gases were obtained in the following manner: A long glazed porcelain tube was so walled into the kiln door that it extended about 0.5 m. into the kiln space. It was attached to a Liebig condenser, which was provided with a U-shaped vessel connected at the curvature with a collecting flask by means of a tube. The condenser and receiver were kept cool by water at from 15° to 20° C., and a current of fire gases was drawn through the whole apparatus during the entire period of a burn by means of a rubber bag provided with valves. In the cooling tube and the receiver a liquid was separated out, colored black by flakes of soot; about 200 grams were obtained from one burn so that there was sufficient material for a chemical determination.

After filtering out the soot, the liquid was colorless and odorless, and of a distinctly acid reaction; the escaping non-condensing gases were odorless when wood was used as a fuel, but with gas firing they had the odor, at times, of sulphurous acid, at times of hydrogen sulphide, according as the burn was an oxidizing or reducing one.

The analyses gave the following results:

Ingredients in 1 liter of water.	Glost burn in wood-kiln May 4th.	Biscuit burn in gas-kiln May 10th.	Biscuit burn in gas-kiln May 11th.	Glost burn in gas-kiln May 16th.
	Gram.	Gram.	Gram.	Gram.
Hydrochloric acid	-	0.039	0.174	0.133
Sulphuric acid	-	0.153	0.318	0.408
Phosphoric acid	-	0.073		
Ferric oxide and alumina	-	0.008	0.022	0.017
Calcium oxide	-	0.011	0.062	0.039
Magnesium oxide	-	0.008	0.020	0.018
Potash	-	} 0.038	0.096	{ 0.037
Soda	-			
Ammonium chloride	-	0.128		{ 0.106 0.047

The precipitated liquid, therefore, contains a number of substances which are able, even if present in small amounts, of exerting a vigorous chemical action on the clay into whose pores they have been absorbed with the help of water. They are either not volatilized by themselves, hence must have gotten into the kiln in the form of dust, or they have a much higher temperature of vaporization, and are concentrated with a rise in temperature, their effect being thus increased, and since the evaporation of water takes place mainly on the surface their activity is chiefly extended to the latter. If we disregard those substances which have probably gotten into the fire gases only in the form of dust, the substances whose action is to be considered chiefly in this connection are the alkaline sulphates, free sulphuric acid, free hydrochloric acid and ammonium chloride. The first three contribute an absolute increase in the amount of salt in the body, since they remain in it or unite with the basic substances of the body as the alkalies, lime, magnesia, ferric oxide, and alumina, and bring them to the surface as salty incrustations which later on at a higher temperature are decomposed again more or less, and give rise either to disfiguring efflorescences or a thin glaze. The alkaline sulphates which we

must imagine as acid salts in the presence of free acid, are known as very active agents for breaking up alumina and iron oxide compounds, and can even decompose a large number of compounds that are not attacked by hot concentrated sulphuric acid; these, too, will be able to bring about decomposition to a considerable depth at such places where they may have been deposited. In a similar manner the ammonium chloride which volatilizes again at 400° C. has a decomposing effect on the silicates of the clay and can cause the formation of volatile chlorides of calcium, magnesium, aluminum, and iron, which, decomposed again, on uniting with water, may deposit at other places. The presence of lime and magnesia, alumina and ferric oxide, as well as of hydrochloric acid, is perhaps wholly or partly to be referred to the simultaneous presence of ammonium chloride in small amounts in the products of combustion. At any rate, a large number of coloring and discoloring phenomena find a natural explanation by the proof of the presence of the above-named substances in the condensed constituents of the fire gases.

### A Draft and Pressure Gauge for Furnaces, and Gas and Air Flues

PROF. CHAS. W. MESLOH, TRANSLATOR

Concerning the importance of the regulation of draft in kilns, a report has been made elsewhere.<sup>1</sup>

Since the fluctuations in the atmospheric pressure and in the temperature, in the direction and intensity of the air currents of the atmosphere, at times retard and again accelerate the progress of the fire in the kilns, it was found that the use of a draft meter enables the burner to regulate the draft by raising or lowering, by opening or closing the damper, and to keep the fire

<sup>1</sup> Dr. Jul. Aron, "A Draft Meter," Notisblatt, 1875, p. 191.

as nearly normal as possible on the basis of a proper gas analysis, and the lack or excess of air supply—identical with waste of fuel—is kept within proper limits.

For the measurement of differences in air pressure we use communicating tubes, filled with liquids, whose one leg is connected by means of tubes with the air chamber in which the pressure is to be measured. The difference of level in the two legs of the communicating tubes gives the amount of pressure above or below that of the pressure of the atmosphere. If the differences in pressure are very small, as in smoke, gas, and air flues, then the difference in level would also be small and very hard to measure, especially for untrained observers. In order to measure slight differences of level in the communicating tubes on an enlarged scale, we make use of the apparatus described below and illustrated by the drawing.

A communicating tube *A*, made out of a calibrated glass tube, widens at its upper ends into two larger glass tubes, *B* and *C*, of equal size. The communicating tube *A B C* is fastened to a board which also carries a scale *D* running parallel to the one leg, and which can be moved up or down by means of the slits *aa* and set screws *bb*. The communicating tube is filled with liquids, which do not mix, of about the same specific gravity, so that their point of contact, *x*, lies in the neighborhood of the zero-point of the scale.

As liquids for filling we may use, for example, water and aniline oil, or petroleum and dilute alcohol, carbolic acid and a water solution of carbolic acid, of which the one liquid is best colored. The apparatus is hung on the wall near the place of observation, and in measuring a pressure higher than that of the

atmosphere the leg *B*, provided with a stopper and glass tube, is brought in connection with the chamber in which the difference of pressure is to be noted by means of rubber, metal, or glass tubes; when a lower pressure is measured the leg *C* is thus connected. The other leg communicates with the atmosphere.

When the apparatus is hung perpendicularly and the scale so set by sliding it in its slits, that its zero-point coincides with the point of contact of the two liquids, and the one leg is connected with a smoke, gas, or air flue, etc., a slight difference will be produced in the level of the liquids in the larger vessels *B* and *C*. The change in level is marked on a larger scale by a change of place of the point of contact of the two non-mixing liquids in the narrow tube *A*, the ratio being the same as the cross-section of the wider vessel to that of the narrow tube.

For example, let the ratio of the cross-sections of the tube *A* and the vessels *B* and *C* be as 1 : 20, then a lowering of the level in *B* by 1 mm. will cause a change of 20 mm. in the point *x*, so that very small differences of level are made very clearly visible.

The division of the scale attached to the apparatus is either an empiric one for relative comparisons, or for more accurate measurements it is based on the pressure of water in millimeters. In the latter case the divisions are calculated from the ratio of the cross-sections of the tube *A* and the vessels *B* and *C*, and the specific gravities of the liquids used for filling.

The apparatus is all the more sensitive and accurate the greater the ratio of the cross-section of the upper vessels is to that of the narrow communicating tube and the less the liquids used for filling vary in specific gravity.

Concerning the use of the apparatus the following is to be noted:\*

After the stoppers have been taken from the apparatus, the communicating tube is filled to the zero point of the scale with

\* The apparatus can be obtained from the chemical laboratory for the clay industries, Berlin N. W., Kruppstr. 6.

the heavier liquid, and then so much of the lighter liquid is added on both sides that the enlarged vessels *B* and *C* are half filled. By the careful addition of drops of the liquid on the one side or the other, there is no trouble in making the point of contact of both liquids coincide with the zero point of the scale.

If in doing this a drop of the upper layer has by chance become separated or *vice versa* of the under layer, it is easy to unite the separated drop with the main body of the liquid by careful sucking or blowing by means of a tube. In replacing the stoppers the glass tube should be held firmly in order that it may not turn since otherwise it will be easily broken. Before using the apparatus it should be set to the zero point by moving the scale; it is also well to test it now and then as to whether the zero point has been changed by evaporation of the liquids. For this purpose the tube is cut off from its connection with the kiln so that both sides of the communicating tube are connected with the atmospheric air. If then the point of contact of the liquids no longer coincides with the zero-point, the scale is either moved in the slits or when this is no longer possible a few drops of the liquid are added on the left side according to need.

It is to be noted that at least so much liquid must be present on the left side of the apparatus, that even when the point of contact of the liquids has been drawn down to the lowest position, there is still some of it left in the cylindrical part of the widened tube on the left side. This follows as a matter of course from the principle of the apparatus since, when the widened tube is completely emptied, there would be left only a simple communicating tube and a magnified depression could not be obtained.

The scale is so calibrated that in filling the apparatus with the liquids mentioned the divisions give directly the water pressure in millimeters.

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## A Trial Kiln for Ceramic Purposes

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PROF. CHAS. W. MESLOH, TRANSLATOR

The results obtained in the chemical investigation of clays, raw materials, glaze bodies, etc., find a useful, practical conclusion only by test burns. These tests supplementary to the analytical result, or for independent experimental purposes, must be as near as possible like the burning on a large scale and it is clear that we will be able to form a better judgment concerning the value of clay bodies, colors, glazes, etc., for practical purposes if these practical experiments, executed on a small scale, agree in their whole course with the process on a large scale. The duration of the burn and the condition of the flame are, therefore, decisive factors for the success of these experiments, and it is especially necessary to be able to adapt them completely to corresponding phenomena on a large scale. A trial kiln useful for ceramic experiments must, therefore, permit us to increase the heat slowly or rapidly at will and to give to the flame an oxidizing or reducing character according to need. At the same time the kiln space proper must have a uniform temperature throughout and to afford the possibility of observing the ware and the pyroscopes set with it without difficulty from the outside.

The kiln illustrated in the accompanying cut originated in the chemical laboratory of the *Thonindustrie-Zeitung*, it answers all the demands made above, and is at all times ready for use and easily managed. It is fired with gas and the greatest part of the air used for combustion is heated by the escaping gases of combustion.

The kiln consists of a thick-walled fire-clay cylinder with a removable lid, which encloses a high fire bridge consisting of a thin-walled cylinder of fire clay. Within the cylindrical fire bridge there is at a short distance from it a fire-clay sagger, *B*,

cylindrical in shape, capable of being closed by a lid, and serving for the reception of the trials to be burned. From eight Bunsen burners, distributed regularly in a circle, the flame enters from without through the thick-walled fire-clay mantle in which corresponding openings have been left, rises along the thin-walled fire bridge, is reflected from the crown and, returning, surrounds the kiln space proper and passes off into the chimney. The air used in combustion enters through the ring-shaped slit remaining between the outer wall and the fire bridge.

When the kiln is to be used, the small inside sagger is first filled with the charge to be burned, and the cones for the degree of heat to be reached, are set in with the charge. Then the opening, supplying air to the Bunsen burners, is closed by turning the iron connecting-ring, the gas cock is slightly opened and the gas ignited. After the lid has been placed in position the opening for the air supply to the Bunsen burners is opened until blue flames are seen.

The cones are observed through a hole in the cover of the sagger and through the peep-hole in the lid of the kiln, loosely closed with a fire-clay stopper.

A larger or smaller supply of gas is obtained by a corre-

sponding opening of the supply cock, and it is therefore possible to cause the temperature to rise rapidly or slowly. If a quick burn is desired cone 010 (melting-point of silver about  $960^{\circ}$  C.) can be melted in thirty to forty minutes, while with slower burning the melting of cone 010 need be accomplished only after several hours.

The kiln was used with advantage for the burning of all kinds of trial pieces, common brick, face brick, pavers, fire-clay ware, faience, white ware, stoneware, cement, magnesite, and porcelain, for the burning of colors and glazes and the production of fluxes and glasses.

If the kiln is to be used for the melting of glaze and color fluxes the fire-clay sagger is exchanged for a so-called Hessian crucible whose bottom is provided with a hole for the tapping off of the liquid mass; as soon as the kiln is red hot the lower cap in the discharge vent is removed and a bucket containing water placed under it which is filled with water high enough so that the tube is immersed several centimeters. The melted glaze or fritt then gradually drops into the water from which it may be taken.

In proportion as the glaze flows from the crucible a new mixture is supplied from above after the lid in the kiln cover has been removed for the time being.<sup>1</sup>

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### Pyrometers and the Measurement of High Temperatures. Standard Cones

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PROF. CHAS. W. MESLOH, TRANSLATOR

More than any other industry, the clay industry demands a careful control of temperature. For instance, in order to melt glass or iron a certain minimum temperature must be reached, exceeding the same causes no appreciable damage in most cases

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<sup>1</sup> A kiln corresponding to the accompanying cut can be obtained from the chemical laboratory of the *Thonindustrie-Zeitung*, Berlin N. W., Kruppstr. 6.

but rather brings about a more rapid effect of the heat. For the burning of clay wares, however, a certain minimum temperature is not only necessary (or a soft burn will result), but a certain maximum must not be exceeded because otherwise the ware will lose its shape and color, change its density, etc. Frequently these two stages of temperature are very close together. In clays containing lime, for example, a slight increase above the admissible temperature at once produces a glass. Hitherto it has been the task of the burner to judge the temperature with his eyes; but even with the most skilful burners mistakes can arise; their eye is not the same at all times, moreover the external illumination plays a very important part in the color of the heat; on bright days it is different than in murky weather, and again different than at night. What means other than the experienced eye of the burner are there available for determining higher degrees of heat?

For the determination of lower temperatures the expansion of mercury furnishes a very good measure as is well known. For the measurement of higher temperatures a mercury apparatus can no longer be used since the glass enclosing the quicksilver is then melted. To measure temperatures by the expansion of air or nitrogen, offers great difficulties because the vessels in which the air must be enclosed undergo changes in volume with the increase in temperature. Platinum, iron, and silver vessels cannot be used since gaseous bodies pass through them at a red heat; glass and porcelain vessels undergo a change of volume at high temperatures so that the volume of the enclosed air can no longer be accurately determined. Moreover, all bodies expand when heated, and even if the coefficients of expansion for low temperatures, for instance,  $100^{\circ}$  or  $200^{\circ}$  have been accurately determined for most bodies, and from this a mathematical correction of the expansion be made, considerable difficulties are still met at higher temperatures, since many bodies expand less between certain temperature limits and more

through others. Some kinds of air thermometer<sup>1</sup> furnish good results for temperatures up to a dark red heat, that is, to 600° C.

The attempts to use the expansion of solid bodies for the determination of temperatures have led to no result. For example, a strip of copper and iron were fastened together. At a low temperature they form a straight rod which however will become bent at a higher temperature, because the copper rod expands more than the iron rod. Since the metals lose their elasticity at high temperatures and thereby change their volume, the rod of copper and iron does not go back to the straight form after cooling but remains bent. For the same reason single metal or carbon rods cannot be used, because after being heated to a high degree they do not return to their former condition on cooling, but are always increased in length to a certain extent. To this class belong the graphite thermometer and the old Wedgwood pyrometer, in which a cube or cylinder of clay was heated in the fire and the temperature inferred from the measurement of the length. In many white ware factories a similar method is used, the temperature required for burning the ware being estimated by the shrinkage which the body of the ware undergoes. Since the slightest difference of the body that is used for the cylindrical measuring pieces changes the whole observation, new calculations must be made for every special material. Probably no one has really seriously thought of introducing this method of measuring temperatures in the clay industries.

The second principle of measuring temperature depends on the change of the state of matter, such as the melting of metals and the like. Especially the melting-points of silver, gold, and platinum which are quite fixed, since the metals are easily obtained in the pure state, have been used early and frequently for this purpose. When gold and silver are alloyed we do not obtain bodies whose melting-points correspond to the average of the composition, but rather such whose melting-points are some-

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<sup>1</sup> Lately also the mercury thermometers filled with nitrogen under pressure.—The editors.

what lower. If the melting-point of silver be taken as 960° C., that of gold as 1075° C., and that of platinum as 1850° C., and assuming the mixtures to possess the average of the melting-points of these we obtain with the mixture of gold and silver for every 10 per cent more of silver a difference of temperature of 11.5° C., and with a mixture of gold and platinum for every 5 per cent more of platinum a difference of 38.75° C. The melting-points indicated by these cannot always be expressed accurately numerically, nevertheless a scale may be arranged from them. The determinations, however, become uncertain as soon as alloys are used that contain more than 20 per cent of platinum since the alloys with the larger percentage of platinum become heterogeneous in melting, that is, on heating, an alloy higher in gold is first segregated out which only gradually takes up the alloy higher in platinum. The temperature corresponding to the melting-point of an alloy of 85 per cent of gold and 15 per cent of platinum would represent about the degree of heat that is used in most brick works. On account of the durability of the alloys this method of measuring temperatures is not expensive.

The attempt has further been made to determine temperatures by means of the phenomena of disassociation. Carbon dioxide begins to be given off by calcium carbonate at 500° C., and decomposition is completed at about 1000°. Between these limits the amount of carbon dioxide given off would enable one to determine the temperature. Since, however, the decomposition depends essentially on the condition in which the calcium carbonate appears whether crystalline or amorphous, and since also the results do not altogether agree this method is completely useless.

Optic and acoustic phenomena have likewise furnished no results that can be used. It has been endeavored to measure the light rays emitted by means of a polarization photometer, to determine the temperature from the color of platinum when glowing, and also from the note given off by a flute when hot fire gases were blown into it. A large number of apparatus which

are intended to determine temperatures from electrical phenomena have already been forgotten.

Better results, perhaps the best for a pyrometer which measures temperatures between wide limits, are given by Siemens's electrical pyrometer. It depends on the fact that the resistance of a platinum wire (a spiral) increases with increasing temperatures and almost proportionately to the temperature so that one can determine not only the temperature limit of the kiln, but also the temperature directly in degrees. It has, however, been observed that when this instrument is repeatedly heated to very high temperatures, the resistance of the platinum wire is changed; hence it must then be standardized anew. This makes the apparatus rather impracticable for factories where people are not always at hand who are trained for such scientific work. Moreover, in its simplest equipment, of wrought iron it has the high price of 400 marks and double the amount when it is made of platinum.

There remains yet the distribution of heat as a measure of temperature. Although many useless pieces of apparatus of this kind have been constructed, yet there are some that furnish very good results. To these belong the calorimeters made by Saintignon and by Fischer. The first instrument consists of two ordinary thermometers which are surrounded by a constant stream of water. The stream of water first surrounds the one thermometer, giving it its temperature, say  $20^{\circ}$ , then the water passes through an iron tube curved like a horseshoe into the kiln in which the water is heated, returns to the second thermometer which registers the temperature there, say  $40^{\circ}$ , and then is discharged. If the water would make no deposits in the heated horseshoe tube, if there were never any smoke in the kiln by which the tube is covered with a layer of soot, keeping off the heat and not burning away, and under the supposition that the water passes through with the same velocity and the same pressure, the difference of temperature would enable one to infer the temperature directly. But as a matter of fact these

suppositions do not correspond with the actual conditions. Fischer's calorimeter is a wooden cup in which there is a copper beaker; the latter is closed above, excepting a small opening for the insertion of a platinum or iron cylinder or a ball. Furthermore there is in the interior a delicate mercury thermometer which is graduated to tenths of degrees, and therefore makes possible the reading of one hundredth degree. The copper beaker is filled with a weighed quantity of water, and also has itself been weighed. Now a weighed iron or platinum cylinder is thrown in which has previously been heated to the temperature of the kiln. Of course the water in the cylinder is heated by it. From the rise in temperature indicated by the thermometer we can calculate the temperature prevailing in the kiln. But also this apparatus is not very practicable in the hands of a workman.

Although silver, gold and platinum with their useful alloys seem best fitted for practical purposes, still the range of the temperatures thus determined is very small and in no way corresponds to the actual needs. For higher temperatures at which the alloys of noble metals are no longer satisfactory or on account of the properties of the alloys no longer offer an accurate means of determination, I have for some time used tetrahedrons made out of porcelain glazes or feldspar which make possible a rather accurate control of the same temperature in burning.

If now, in order to follow a proposition made by Dr. Heintz, of Saarau, we disregard the determination of temperature according to the ordinary conception of degrees for the purposes of the ceramic industries, we can put in its place a series of tetrahedrons made out of glazes which melt down, one after the other, and infer the temperature attained from the number of tetrahedrons which have melted or express the attainment of a certain temperature in the kiln by the melting of a definite glaze.

This process would be analogous to that of measuring light by means of standard candles, *i. e.*, candles of definite dimensions, definite wick construction, definite consumption of the

substance maintaining the combustion per unit of time. The light of such candles, always made in the same manner at the same place, form the unit of measure; here the question would be one of making definite glazes with as uniform a composition as possible out of the same raw materials at the same place and to use their melting-points for the determination of the temperatures attained in the kiln.

In the making of such a series of consecutively melting glazes my first consideration must, of necessity, have been to select raw materials for the production of the glazes, in order, on the one hand, that they might be of constant composition, on the other hand, that they should be stable in the fire and make possible an exact composition. The making of ordinary glasses for this purpose was not considered, because it is impossible to protect the raw materials used for their production from the attack of the crucible in which they are melted, and also because in melting much of the alkali is volatilized. According to Stein the loss of alkali in melting glass amounts to 16 per cent, and according to Splittergerber 11 to 40 per cent; thus it would be impossible to produce bodies of the same composition and hence of the same melting-point. The use of boracic acid and lead glazes was also not considered at first. Furthermore, cones made from fused glasses have the property of softening slowly. Liquefaction takes place very gradually, the change in shape is extended over a rather long space of time, and hence the determination of temperatures becomes uncertain; in addition, many glasses devitrify, that is, segregate out crystalline particles on slow heating, such as they experience in the kilns of the clay industry. This devitrification disappears only at a temperature above that of first softening when the glass has attained a certain degree of liquidity so that the melting silicates do not show definitely the first stage of fusion, which alone is of importance. Accordingly I chose the ingredients which serve for the production of porcelain glazes on a large scale (that is, feldspar, calcium carbonate, quartz, and kaolin), because these

on the one hand, occur in nature in a nearly definite composition, and on the other hand, because they contain no substances to be volatilized, and hence are the first materials to be considered as regards the maintenance of a constant composition.

At the same time I was compelled to neglect the production of glazes of a very low melting-point, because these substances make possible only more difficultly fusible glasses. For lower, temperatures some further work must be done.

In the following I give the analyses of those constituents of the glaze cones which I have used in this work:

	Roerstrand feldspar from Becker, Stettin	Zettlitz kaolin, from Fischer and Mieg.	Norwegian quartz, from Becker, Stettin.	Marble from Carrara.
Silica - - -	64.32	46.87	98.52	1.00
Alumina - - -	19.41	38.56	1.04}	0.12
Iron oxide - - -	0.14	0.83	0.01}	
Lime - - -	trace	trace		54.93
Magnesia - - -	0.35	trace		0.21
Potash - - -	12.90}		0.40	
Soda - - -	2.10}	1.06		
Loss on ignition - -	0.57	12.73		
Carbon dioxide -	—	—	—	43.76
	99.74	100.05	100.00	100.02

In the feldspar which may be considered as the purest one, most uniformly reliable in regard to natural occurrence, the ratio of fluxing bases : alumina : silica = 1 : 1.09 : 6.19, compared with the theoretical, 1 : 1.00 : 6.00.

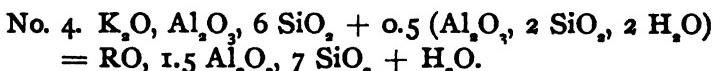
The Zettlitz kaolin, almost pure clay substance with only 1.5 per cent of quartz, has the ratio of alumina (+ iron oxide) : silica = 1 : 2.08 (theoretical 1 : 2). The quartz and marble are also almost pure substances, the first with 98.52 per cent of silica, the latter with 98.88 per cent of calcium carbonate.

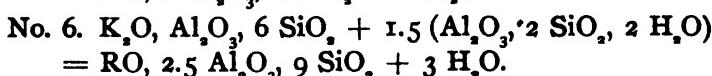
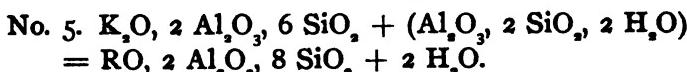
The substances were considered as chemically pure for this work, the theoretical ratios being used in the calculation of the glazes.

I at first expected to arrive at lower or higher melting glazes, as compared with the feldspar used in the easiest way by increasing, on the one hand, the quantity of fluxes by adding calcium carbonate (marble from Carrara), on the other hand, by decreasing the quantity of fluxes through the addition of Zettlitz kaolin or quartz. But this proved entirely unsuitable, because the phenomena of fusion connected with this practice stand in contradiction with the previous views held by us in regard to the influence of these constituents upon the fusibility. If one equivalent of feldspar, or 278.5 parts, is compounded with 1, 2, 3 equivalents of calcium carbonate, or 50, 100, 150 parts, there are obtained, collecting potash and lime as fluxes under the common designation of RO, the following mixtures:

- No. 1.  $K_2O, Al_2O_3, 6 SiO_2 + CaO, CO_2$   
 $= RO, 0.5 Al_2O_3, 3 SiO_2 + CO_2$
- No. 2.  $K_2O, Al_2O_3, 6 SiO_2 + 2 CaO, CO_2$   
 $= RO, 0.33 Al_2O_3, 2 SiO_2 + 2 CO_2$
- No. 3.  $K_2O, Al_2O_3, 6 SiO_2 + 3 CaO, CO_2$   
 $= RO, 0.25 Al_2O_3, 1.5 SiO_2 + 3 CO_2$

According to the views previously held, the assumption had to be made that these compounds are more fusible than the feldspar, for they possess a higher content of fluxes, and less alumina and silica. While the feldspar is a sixfold silicate with one equivalent of alumina these compounds represent a trisilicate, a bisilicate and a one and a half silicate, with only a half, a third, and a fourth equivalent of alumina. These mixtures, however, all proved more infusible than the feldspar, and the more so, the lower the content of silica and alumina. No. 3 was yet completely porous at a temperature at which the pure feldspar still already fused to a liquid mass. The mixtures of feldspar with Zettlitz kaolin behaved similarly.





These mixtures likewise possessed a higher melting-point than feldspar, which increased with an increase in the content of Zettlitz kaolin. In the same way the melting-point of feldspar was raised as soon as quartz was added to it.

Matters, however, appeared different as soon as both calcium carbonate and kaolin were added to the feldspar. There resulted mixtures whose melting-points were immediately lowered.

In order to determine the proportions of mixing the feldspar, marble, kaolin, and quartz, whenever the latter was needed, a number of glaze mixtures were prepared. These were mixed from finely powdered and dried raw materials, intimately rubbed on a glass plate and from the mixture tetrahedrons were molded in oiled copper molds. The tetrahedrons were 6 cm. high, each side of the triangular base being 1.5 cm.; these were finally cemented to a fire-clay tile and exposed to the fusing heat of feldspar. In the following table, in column 2 will be found the composition of the glaze mixtures, in column 3 their chemical formulas, in column 4 the appearance of the cones at the melting heat of the feldspar.

These are divided into eight groups. The first group contains feldspar and quartz in the equivalent proportion of 1 : 6, and the clay content rises from  $\frac{1}{2} : \frac{1}{2}$  equivalent.

In the next three groups they have a composition similar to that of the members of the first group, designated by letters, only with an addition of 1, 2, 3 equivalents of calcium carbonate.

The members in the groups 5-8 have the same composition as in the first groups, only in place of 6 we have 12 equivalents of carbon dioxide. The relatively most fusible mixtures in every group are always marked with a †.

	I	Feldspar	278.5	K <sub>2</sub> O, Al <sub>2</sub> O <sub>3</sub> , 12 SiO <sub>2</sub>	
	6	Quartz	180.0		† Not melted. Resembling porcelain.
	I	" Feldspar	278.5		
	6	" Quartz	180.0	K <sub>2</sub> O, Al <sub>2</sub> O <sub>3</sub> , 13 SiO <sub>2</sub>	
	0.5	" Zettl. kaol.	64.75		
	I	" Feldspar	278.5		
	6	" Quartz	180.0	K <sub>2</sub> O, Al <sub>2</sub> O <sub>3</sub> , 14 SiO <sub>2</sub>	
	I	" Zettl. kaol.	129.5		Test cone sharp cornered, with increasing additions of kaolin, the exterior gloss and the transparency decrease.
	I	" Feldspar	278.5		
	6	" Quartz	180.0	K <sub>2</sub> O, Al <sub>2</sub> O <sub>3</sub> , 15 SiO <sub>2</sub>	
	1.5	" Zettl. kaol.	194.25		
	I	" Feldspar	278.5		
	2	Quartz	180.0	0.5K <sub>2</sub> O } 0.5Al <sub>2</sub> O <sub>3</sub> , 6 SiO <sub>2</sub>	Melted to round drops.
	I	Marble	50.00	0.5CaO }	
	I	" Feldspar	278.5		
	2a	Quartz	180.0	0.5K <sub>2</sub> O } 0.75Al <sub>2</sub> O <sub>3</sub> , 6.50 SiO <sub>2</sub>	† Melted to round drops. The softest glaze falls in this group.
	I	Marble	50.00	0.5CaO }	
	0.5	" Zettl. kaol.	64.75		
	I	" Feldspar	278.5		
	2b	Quartz	180.0	0.5K <sub>2</sub> O } 1.00Al <sub>2</sub> O <sub>3</sub> , 7.00 SiO <sub>2</sub>	Gone down, but the shape of the cone is still recognizable.
	I	Marble	50.00	0.5CaO }	
	I	" Zettl. kaol.	129.5		
	I	" Feldspar	278.5		
	2c	Quartz	180.0	0.5K <sub>2</sub> O } 1.25Al <sub>2</sub> O <sub>3</sub> , 7.50 SiO <sub>2</sub>	Not gone down.
	I	Marble	50.00	0.5CaO }	
	I.5	" Zettl. kaol.	194.25		
	I	" Feldspar	278.5		
	3	Quartz	180.00	0.33K <sub>2</sub> O } 0.33Al <sub>2</sub> O <sub>3</sub> , 4.00 SiO <sub>2</sub>	Gone down, but the shape of the cone is still recognizable, inclined to devitrification.
	2	Marble	100.00	0.66CaO }	
	I	" Feldspar	278.5		
	3a	Quartz	180.00	0.33K <sub>2</sub> O } 0.50Al <sub>2</sub> O <sub>3</sub> , 4.33 SiO <sub>2</sub>	† Melted down level
	2	Marble	100.00	0.66CaO }	
	0.5	" Zettl. kaol.	64.75		
	I	" Feldspar	278.5		
	3b	Quartz	180.0	0.33K <sub>2</sub> O } 0.66Al <sub>2</sub> O <sub>3</sub> , 4.66 SiO <sub>2</sub>	Down flat, approximately the same melting-point as in the preceding.
	2	Marble	100.00	0.66CaO }	
	I	" Zettl. kaol.	129.5		
	I	" Feldspar	278.5		
	3c	Quartz	180.0	0.33K <sub>2</sub> O } 0.83Al <sub>2</sub> O <sub>3</sub> , 5 SiO <sub>2</sub>	Gone down, but the form of the cone still recognizable.
	2	Marble	100.00	0.66CaO }	
	I.5	" Zettl. kaol.	194.25		
	I	" Feldspar	278.5		
	4	Quartz	180.00	0.25K <sub>2</sub> O } 0.25Al <sub>2</sub> O <sub>3</sub> , 3 SiO <sub>2</sub>	Cone has settled, but is not entirely gone down.
	3	Marble	150.00	0.75CaO }	

4a	1	Eq. Feldspar	278.5	$K_2O, 0.25K_2O \} 0.38Al_2O_3, 3.25SiO_2$	Melted into a drop-like mass; has an inclination to devitrification.	
	6	" Quartz	180.00			
	3	" Marble	150.00			
	0.5	" Zettl. kaol.	64.75			
4b	1	" Feldspar	278.5	$K_2O, 0.25K_2O \} 0.5Al_2O_3, 3.5SiO_2$	↑ Melted down flat. Has begun to clear.	
	6	" Quartz	180.00			
	3	" Marble	150.00			
	1	" Zettl. kaol.	129.5			
4c	1	" Feldspar	278.5	$K_2O, 0.25K_2O \} 0.63Al_2O_3, 3.75SiO_2$	Melted down flat. Shows tendency to devitrification.	
	6	" Quartz	180.00			
	3	" Marble	150.00			
	1.5	" Zettl. kaol.	194.25			
5	5	1 "	Feldspar	278.5	$K_2O, Al_2O_3, 18SiO_2$	†
	12	" Quartz	360.00			
	5a	1 "	Feldspar	278.5		
	12	" Quartz	360.00			
5b	0.5	" Zettl. kaol.	64.75	$K_2O, 1.5Al_2O_3, 19SiO_2$	Not melted, resembling porcelain less glazed than the mixture carried out under 5.	
	1	" Feldspar	278.5			
	12	" Quartz	360.00			
	1	" Zettl. kaol.	129.5			
5c	5c	1 "	Feldspar	278.5	$K_2O, 2.5Al_2O_3, 21SiO_2$	]
	12	" Quartz	360.00			
	1.5	" Zettl. kaol.	194.25			
	6	1 "	Feldspar	278.5	$K_2O, 0.5CaO \} 0.5Al_2O_3, 9SiO_2$	Melted down, but the form is still plainly recognizable.
6a	12	" Quartz	360.00			
	1	" Marble	50.00			
	1	" Feldspar	278.5	$K_2O, 0.5CaO \} 0.75Al_2O_3, 9.5SiO_2$	† Melted down to round drops.	
	12	" Quartz	360.00			
6b	1	" Marble	50.00			
	0.5	" Zettl. kaol.	64.75			
	1	" Feldspar	278.5			
	12	" Quartz	360.00			
6c	1	" Marble	50.00	$K_2O, 0.5CaO \} 1.0Al_2O_3, 10SiO_2$	Less strongly fused than 6.	
	1	" Zettl. kaol.	129.5			
	1	" Feldspar	278.5			
	12	" Quartz	360.00			
7	1	" Marble	50.00	$K_2O, 0.5CaO \} 1.25Al_2O_3, 10.5SiO_2$	Cone with a bent point.	
	1.5	" Zettl. kaol.	194.25			
	2	" Feldspar	278.5			
	12	" Quartz	360.00	$K_2O, 0.33Al_2O_3, 6SiO_2$		
	2	" Marble	100.00			
	7	" Feldspar	278.5	$K_2O, 0.66CaO \} 0.33Al_2O_3, 6SiO_2$	Melted down, but with form still recognizable.	

7a	1	Eq. Feldspar	278.5		
	12	" Quartz	360.000.33 K <sub>2</sub> O } 0.5 CaO } 0.5 Al <sub>2</sub> O <sub>3</sub> , 6.33 SiO <sub>2</sub>	Melted down to round drops.	
	2	" Marble	100.000.66 CaO }		
	0.5	" Zettl. kaol.	64.5		
7b	1	" Feldspar	278.5		
	12	" Quartz	360.000.33 K <sub>2</sub> O } 0.66 CaO }	† Has flowed together into round drops.	
	2	" Marble	100.000.66 CaO }		
	1	" Zettl. kaol.	129.5		
7c	1	" Feldspar	278.5		
	12	" Quartz	360.000.33 K <sub>2</sub> O } 0.83 CaO }	Melted into round drops.	
	2	" Marble	100.000.66 CaO }		
	1.5	" Zettl. kaol.	194.25		
8	1	" Feldspar	278.5		
	12	" Quartz	360.000.25 K <sub>2</sub> O } 0.75 CaO }	Melted into round drops.	
	3	" Marble	150.000.75 CaO }		
8a	1	" Feldspar	278.5		
	12	" Quartz	360.000.25 K <sub>2</sub> O } 0.38 CaO }	Melted down into round drops.	
	3	" Marble	150.000.75 CaO }		
	0.5	" Zettl. kaol.	64.75		
8b	1	" Feldspar	278.5		
	12	" Quartz	360.000.25 K <sub>2</sub> O } 0.50 CaO }	† Melted down into round drops which have begun to clear.	
	3	" Marble	150.000.75 CaO }		
	1	" Zettl. kaol.	129.5		
8c	1	" Feldspar	278.5		
	12	" Quartz	360.000.25 K <sub>2</sub> O } 0.63 CaO }	Melted down into round drops which have begun to clear.	
	3	" Marble	150.000.75 CaO }		
	1.5	" Zettl. kaol.	194.25		

Selecting the most easily fusible mixtures, and neglecting those of groups 1 and 5 which do not show any fusion at the melting heat of feldspar, they will be found to be the following, chosen from the several groups:

From group 2 -	0.5 K <sub>2</sub> O } 0.75 Al <sub>2</sub> O <sub>3</sub> , 6.5 SiO <sub>2</sub> . 0.5 CaO }
From group 3 -	0.33 K <sub>2</sub> O } 0.5 Al <sub>2</sub> O <sub>3</sub> , 4.33 SiO <sub>2</sub> . 0.56 CaO }
From group 4 -	0.25 K <sub>2</sub> O } 0.5 Al <sub>2</sub> O <sub>3</sub> , 3.5 SiO <sub>2</sub> . 0.75 CaO }
From group 6 -	0.5 K <sub>2</sub> O } 0.75 Al <sub>2</sub> O <sub>3</sub> , 9.5 SiO <sub>2</sub> . 0.5 CaO }
From group 7 -	0.33 K <sub>2</sub> O } 0.66 Al <sub>2</sub> O <sub>3</sub> , 6.66 SiO <sub>2</sub> . 0.60 CaO }
From group 8 -	0.25 K <sub>2</sub> O } 0.5 Al <sub>2</sub> O <sub>3</sub> , 5 SiO <sub>2</sub> . 0.75 CaO }

The relatively most fusible mixtures taken from these groups are those from the groups 4 and 8, which at the temperature used (melting-point of feldspar) already commenced to become clear, having thus attained a considerable degree of liquidity. From this it appears distinctly that neither the glazes lowest in alumina are really the most fusible ones, nor those with a higher content of alkali, but that for low fusibility, there must evidently be a definite proportion between alumina and fluxes. This relation becomes still more distinct in the following experiments in which the fluxes (RO) always had the same composition (0.2 K<sub>2</sub>O, 0.8 CaO), but the alumina and silica content was increased. Mixtures were again prepared and burned at the same temperature whereby in every group the going down of the most easily fusible cones was observed.

	Feldspar	55.7		
9	Marble	40.0	RO, 0.2 Al <sub>2</sub> O <sub>3</sub> , 2 SiO <sub>2</sub> .	
	Quartz	24.0		
	Feldspar	55.7		
9a	Marble	40.0	RO, 0.3 Al <sub>2</sub> O <sub>3</sub> , 2 SiO <sub>2</sub> .	
	Quartz	18.00		
	Zettlitz kaolin	12.9		
	Feldspar	55.7		
9b	Marble	40.00	RO, 0.4 Al <sub>2</sub> O <sub>3</sub> , 2 SiO <sub>2</sub> .	
	Quartz	12.0		
	Zettlitz kaolin	25.9		
	Feldspar	55.7		
9c	Marble	40.00	RO, 0.5 Al <sub>2</sub> O <sub>3</sub> , 2 SiO <sub>2</sub> . †	
	Quartz	6.0		
	Zettlitz kaolin	38.8		
	Feldspar	55.7		
9d	Marble	40.0	RO, 0.6 Al <sub>2</sub> O <sub>3</sub> , 2 SiO <sub>2</sub> .	
	Zettlitz kaolin	51.8		
	Feldspar	55.7		
10	Marble	40.0	RO, 0.2 Al <sub>2</sub> O <sub>3</sub> , 3 SiO <sub>2</sub> .	
	Quartz	54.0		
	Feldspar	55.7		
10a	Marble	40.0	RO, 0.3 Al <sub>2</sub> O <sub>3</sub> , 3 SiO <sub>2</sub> .	
	Quartz	48.0		
	Zettlitz kaolin	12.9		
				This group showed

10b	Feldspar Marble Quartz Zettlitz kaolin	55.7 40.0 42.0 25.9	RO, 0.4 Al <sub>2</sub> O <sub>3</sub> , 3 SiO <sub>2</sub> .	itself more easily fusible than the preceding, but was more difficultly fusible than the following group. Glaze No. 10c is the easiest fused.
10c	Feldspar Marble Quartz Zettlitz kaolin	55.7 40.0 36.0 38.8	RO, 0.5 Al <sub>2</sub> O <sub>3</sub> , 3 SiO <sub>2</sub> . †	
10d	Feldspar Marble Quartz Zettlitz kaolin	55.7 40.0 30.0 51.8	RO, 0.6 Al <sub>2</sub> O <sub>3</sub> , 3 SiO <sub>2</sub> .	
11	Feldspar Marble Quartz	55.7 40.0 84.0	RO, 0.2 Al <sub>2</sub> O <sub>3</sub> , 4 SiO <sub>2</sub> .	
11a	Feldspar Marble Quartz Zettlitz kaolin	55.7 40.0 78.0 12.9	RO, 0.3 Al <sub>2</sub> O <sub>3</sub> , 4 SiO <sub>2</sub> .	This group was still more fusible than the preceding; the easiest fused was 11c.
11b	Feldspar Marble Quartz Zettlitz kaolin	55.7 40.0 72.0 25.9	RO, 0.4 Al <sub>2</sub> O <sub>3</sub> , 4 SiO <sub>2</sub> .	
11c	Feldspar Marble Quartz Zettlitz kaolin	55.7 40.0 66.0 38.8	RO, 0.5 Al <sub>2</sub> O <sub>3</sub> , 4 SiO <sub>2</sub> . †	
11d	Feldspar Marble Quartz Zettlitz kaolin	55.7 40.0 60.0 51.8	RO, 0.6 Al <sub>2</sub> O <sub>3</sub> , 4 SiO <sub>2</sub> .	
12	Feldspar Marble Quartz	55.7 40.0 114.0	RO, 0.2 Al <sub>2</sub> O <sub>3</sub> , 5 SiO <sub>2</sub> .	
12a	Feldspar Marble Quartz Zettlitz kaolin	55.7 40.0 108.0 12.9	RO, 0.3 Al <sub>2</sub> O <sub>3</sub> , 5 SiO <sub>2</sub> .	
12b	Feldspar Marble Quartz Zettlitz kaolin	55.7 40.0 102.0 25.9	RO, 0.4 Al <sub>2</sub> O <sub>3</sub> , 5 SiO <sub>2</sub> .	This group is less fusible than the glazes of the preceding group; the glazes 12c and 12d were the most fusible, and showed no recognizable difference.
12c	Feldspar Marble Quartz Zettlitz kaolin	55.7 40.0 96.0 38.8	RO, 0.5 Al <sub>2</sub> O <sub>3</sub> , 5 SiO <sub>2</sub> . †	

12d	Feldspar Marble Quartz Zettlitz kaolin	55.7 40.0 90.0 51.8	RO, 0.6 Al <sub>2</sub> O <sub>3</sub> , 5 SiO <sub>2</sub> .	
13	Feldspar Marble Quartz	55.7 40.0 144.0	RO, 0.2 Al <sub>2</sub> O <sub>3</sub> , 6 SiO <sub>2</sub> .	
13a	Feldspar Marble Quartz Zettlitz kaolin	55.7 40.0 138.0 12.9	RO, 0.3 Al <sub>2</sub> O <sub>3</sub> , 6 SiO <sub>2</sub> .	
13b	Feldspar Marble Quartz Zettlitz kaolin	55.7 40.0 132.0 25.9	RO, 0.4 Al <sub>2</sub> O <sub>3</sub> , 6 SiO <sub>2</sub> .	This group is less fusible than the glazes of the preceding group; the most fusible were 13c and 13d, which went down almost at the same time.
13c	Feldspar Marble Quartz Zettlitz kaolin	55.7 40.0 126.0 38.8	RO, 0.5 Al <sub>2</sub> O <sub>3</sub> , 6 SiO <sub>2</sub> . †	
13d	Feldspar Marble Quartz Zettlitz kaolin	55.7 40.0 120.0 51.8	RO, 0.6 Al <sub>2</sub> O <sub>3</sub> , 6 SiO <sub>2</sub> .	

When these trials were burned in groups, as they are given in the preceding pages, each group having thus the same content of fluxes and silica but an increasing content of alumina, the tests, at the melting heat of feldspar, with the lowest percentage of alumina always showed sharp edges, and were hardly translucent along the edges and quite porous, while the fusibility was increased with an increase in alumina; with 0.5 equivalent alumina maximum fusibility was reached, and above that the melting-point again began to rise. This phenomenon was bound to appear remarkable since hitherto it had always been assumed that the glasses and glazes with the lowest content of alumina were the most fusible ones. This behavior is important, not only for the clay industry, which endeavors to produce as fusible glazes as possible, but also for the glass industry, which for ordinary bottles demands a similar aluminous glass as does the porcelain industry for its glazes. When the separate trials were

so arranged to groups, that they possess the same content of fluxes and the same content of alumina, the groups thus comprising 9, 10, 11, 12, 13, and again 9a, 10a, 11a, 12a, 13a, the amount of silica rises steadily within these groups. The trials of the separate groups burned at the melting heat of feldspar showed differences in fusibility among themselves but these were only slight. However, as a whole, the single group showed a considerable variation in fusibility according to its content of alumina. In general, the most fusible glazes were 9c, 10c, 11c, 12c, 13c, and among these cone 11c was first melted, representing a glaze of the composition :  $\left\{ \begin{array}{l} 0.2 \text{ K}_2\text{O} \\ 0.8 \text{ CaO} \end{array} \right\} 0.5 \text{ Al}_2\text{O}_3, 4 \text{ SiO}_2$ .

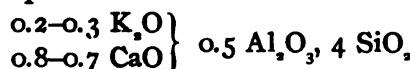
After the most suitable relation of alumina and silica was thus determined for the most fusible glaze, there remained yet to be determined what favorable proportion between the fluxes, potash, and lime is to be accepted in order to keep the glaze as fusible as possible. For this purpose the glaze RO,  $0.5 \text{ Al}_2\text{O}_3, 4 \text{ SiO}_2$ , was so changed that RO was represented by CaO,  $\left\{ \begin{array}{l} 0.1 \text{ K}_2\text{O} \\ 0.9 \text{ CaO} \end{array} \right\}$   
 $\left\{ \begin{array}{l} 0.2 \text{ K}_2\text{O} \\ 0.8 \text{ CaO} \end{array} \right\} \left\{ \begin{array}{l} 0.3 \text{ K}_2\text{O} \\ 0.7 \text{ CaO} \end{array} \right\} \left\{ \begin{array}{l} 0.4 \text{ K}_2\text{O} \\ 0.6 \text{ CaO} \end{array} \right\} \text{ and } \left\{ \begin{array}{l} 0.5 \text{ K}_2\text{O} \\ 0.5 \text{ CaO} \end{array} \right\}$

This produced the following mixtures:

	Marble	50.0	
14	Quartz	90.0	CaO, $0.5 \text{ Al}_2\text{O}_3, 4 \text{ SiO}_2$ ,
	Zettilitz kaolin	64.7	
	Feldspar	27.8	
14a	Marble	45.0	$0.1 \text{ K}_2\text{O} \right\} 0.5 \text{ Al}_2\text{O}_3, 4 \text{ SiO}_2$ ,
	Quartz	78.0	$0.9 \text{ CaO} \right\}$
	Zettilitz kaolin	51.8	
	Feldspar	55.7	
14b	Marble	40.0	$0.2 \text{ K}_2\text{O} \right\} 0.5 \text{ Al}_2\text{O}_3, 4 \text{ SiO}_2$ ,
	Quartz	66.0	$0.8 \text{ CaO} \right\}$
	Zettilitz kaolin	38.8	
	Feldspar	83.6	
14c	Marble	35.0	$0.3 \text{ K}_2\text{O} \right\} 0.5 \text{ Al}_2\text{O}_3, 4 \text{ SiO}_2$ ,
	Quartz	54.0	$0.7 \text{ CaO} \right\}$
	Zettilitz kaolin	25.9	

14d	Feldspar	111.4	
	Marble	30.0	0.4 K <sub>2</sub> O }
	Quartz	42.0	0.6 CaO }
	Zettlitz kaolin	12.9	0.5 Al <sub>2</sub> O <sub>3</sub> , 4 SiO <sub>2</sub> .
14e	Feldspar	139.3	0.5 K <sub>2</sub> O }
	Marble	25.0	0.5 CaO }
	Quartz	30.0	0.5 Al <sub>2</sub> O <sub>3</sub> , 4 SiO <sub>2</sub> .

When these six mixtures were heated to the melting heat of feldspar, the trials 14b and 14c went down first and almost simultaneously, far below the temperature reached, and after the experiment were found to show a tendency to become clear. Then 14a and 14d melted, and the tests 14 and 14e were left as porcelain-like bodies without any appreciable fusion on the edges. Therefore, the proportion between the fluxes K<sub>2</sub>O and CaO from 0.2-0.3 to 0.8-0.7 must be considered as the most favorable one for fusion. The most fusible true porcelain glaze at all producible in this manner, from the raw materials mentioned, has thus the composition :



Of these the second composition was chosen.

This glaze, according to its equivalent proportion of silica was numbered 4, and it was now endeavored to produce glazes still more fusible by replacing part of the alumina by iron oxide. This attempt was quite successful when up to 0.2 equivalent of the alumina in the above glaze was replaced by equivalent quantities of Fe<sub>2</sub>O<sub>3</sub>. On increasing the iron content still more devitrifying glazes were obtained which, of course, could not be considered. On the other hand, more infusible glazes were produced by a further increase of the alumina and silica content. In order not to complicate the conditions it was decided, beginning with glaze No. 5 which contains ten times as much silica as alumina in equivalents, to retain this proportion; thus in these the alumina equivalent stands to the silica equivalent in the ratio of 1 : 10.

The following mixtures were now made for the standard

cones. These mixtures after weighing were put into small porcelain ball mills and ground in water for half a day for the purpose of intimate blending. The slip after decanting as much water as possible was evaporated to dryness and then thoroughly worked with mucilage water. From the mass thus produced tetrahedrons, 6 cm. high with a base whose sides are  $1\frac{1}{2}$  cm. in length, were molded. In the following tables I give the chemical formulas as well as the composition of the standard cones :

No.	Chemical formula.	Mixture.	
1	$0.3 \text{ K}_2\text{O} \} \quad \{ 0.2 \text{ Fe}_2\text{O}_3 \} \quad 4 \text{ SiO}_2$ $0.7 \text{ CaO} \} \quad \{ 0.3 \text{ Al}_2\text{O}_3 \}$	Feldspar      83.55 Marble        35.00 Quartz        66.00 Iron oxide    16.00	
2	$0.3 \text{ K}_2\text{O} \} \quad \{ 0.1 \text{ Fe}_2\text{O}_3 \} \quad 4 \text{ SiO}_2$ $0.7 \text{ CaO} \} \quad \{ 0.4 \text{ Al}_2\text{O}_3 \}$	Feldspar      83.55 Marble        35.00 Quartz        60.00 Iron oxide    8.0 Zettlitz kaolin    12.95	
3	$0.3 \text{ K}_2\text{O} \} \quad \{ 0.05 \text{ Fe}_2\text{O}_3 \} \quad 4 \text{ SiO}_2$ $0.7 \text{ CaO} \} \quad \{ 0.45 \text{ Al}_2\text{O}_3 \}$	Feldspar      83.55 Marble        35.00 Quartz        57.00 Iron oxide    4.00 Zettlitz kaolin    19.43	
4	$0.3 \text{ K}_2\text{O} \} \quad 0.5 \text{ Al}_2\text{O}_3, \quad 4 \text{ SiO}_2$ $0.7 \text{ CaO} \}$	Feldspar      83.55 Marble        35.00 Quartz        54.00 Zettlitz kaolin    25.90	
5	$0.3 \text{ K}_2\text{O} \} \quad 0.5 \text{ Al}_2\text{O}_3, \quad 5 \text{ SiO}_2$ $0.7 \text{ CaO} \}$	Feldspar      83.55 Marble        35.00 Quartz        84.00 Zettlitz kaolin    25.90	Difference in com-
6	$0.3 \text{ K}_2\text{O} \} \quad 0.6 \text{ Al}_2\text{O}_3, \quad 6 \text{ SiO}_2$ $0.7 \text{ CaO} \}$	Feldspar      83.55 Marble        35.00 Quartz        108.0 Zettlitz kaolin    38.85	

No.	Chemical formula.	Mixture.	
7	$0.3 \text{K}_2\text{O} \left\{ \begin{array}{l} \\ \end{array} \right. 0.7 \text{CaO} \} 0.7 \text{Al}_2\text{O}_3, 7 \text{SiO}_2$	Feldspar 83.55 Marble 35.00 Quartz 132.00 Zettlitz kaolin 51.80	position is 0.1 $\text{Al}_2\text{O}_3$ , 1.0 $\text{SiO}_2$ .
8	$0.3 \text{K}_2\text{O} \left\{ \begin{array}{l} \\ \end{array} \right. 0.7 \text{CaO} \} 0.8 \text{Al}_2\text{O}_3, 8 \text{SiO}_2$	Feldspar 83.55 Marble 35.00 Quartz 156.00 Zettlitz kaolin 64.75	
9	$0.3 \text{K}_2\text{O} \left\{ \begin{array}{l} \\ \end{array} \right. 0.7 \text{CaO} \} 0.9 \text{Al}_2\text{O}_3, 9 \text{SiO}_2$	Feldspar 83.55 Marble 35.00 Quartz 180.00 Zettlitz kaolin 77.70	
10	$0.3 \text{K}_2\text{O} \left\{ \begin{array}{l} \\ \end{array} \right. 0.7 \text{CaO} \} 1.0 \text{Al}_2\text{O}_3, 10 \text{SiO}_2$	Feldspar 83.55 Marble 35.00 Quartz 204.00 Zettlitz kaolin 90.65	
11	$0.3 \text{K}_2\text{O} \left\{ \begin{array}{l} \\ \end{array} \right. 0.7 \text{CaO} \} 1.2 \text{Al}_2\text{O}_3, 12 \text{SiO}_2$	Feldspar 83.55 Marble 35.00 Quartz 252.00 Zettlitz kaolin 116.55	Difference in composition is 0.2 $\text{Al}_2\text{O}_3$ , 2.0 $\text{SiO}_2$ ,
12	$0.3 \text{K}_2\text{O} \left\{ \begin{array}{l} \\ \end{array} \right. 0.7 \text{CaO} \} 1.4 \text{Al}_2\text{O}_3, 14 \text{SiO}_2$	Feldspar 83.55 Marble 35.00 Quartz 300.00 Zettlitz kaolin 142.45	
13	$0.3 \text{K}_2\text{O} \left\{ \begin{array}{l} \\ \end{array} \right. 0.7 \text{CaO} \} 1.6 \text{Al}_2\text{O}_3, 16 \text{SiO}_2$	Feldspar 83.55 Marble 35.00 Quartz 348.00 Zettlitz kaolin 168.35	
14	$0.3 \text{K}_2\text{O} \left\{ \begin{array}{l} \\ \end{array} \right. 0.7 \text{CaO} \} 1.8 \text{Al}_2\text{O}_3, 18 \text{SiO}_2$	Feldspar 83.55 Marble 35.00 Quartz 396.00 Zettlitz kaolin 194.25	
15	$0.3 \text{K}_2\text{O} \left\{ \begin{array}{l} \\ \end{array} \right. 0.7 \text{CaO} \} 2.1 \text{Al}_2\text{O}_3, 21 \text{SiO}_2$	Feldspar 83.55 Marble 35.00 Quartz 468.00 Zettlitz kaolin 233.10	Difference in com-
16	$0.3 \text{K}_2\text{O} \left\{ \begin{array}{l} \\ \end{array} \right. 0.7 \text{CaO} \} 2.4 \text{Al}_2\text{O}_3, 24 \text{SiO}_2$	Feldspar 83.55 Marble 35.00 Quartz 540.00 Zettlitz kaolin 271.95	0.3 $\text{Al}_2\text{O}_3$ ,

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No.	Chemical formula.	Mixture.	Position 3.0 SiO <sub>2</sub> , is
17	0.3 K <sub>2</sub> O } 0.7 CaO } 2.7 Al <sub>2</sub> O <sub>3</sub> , 27 SiO <sub>2</sub>	Feldspar 83.55 Marble 35.00 Quartz 612.00 Zettlitz kaolin 310.80	
18	0.3 K <sub>2</sub> O } 0.7 CaO } 3.1 Al <sub>2</sub> O <sub>3</sub> , 31 SiO <sub>2</sub>	Feldspar 83.55 Marble 35.00 Quartz 708.00 Zettlitz kaolin 362.60	Difference in composition 0.4 Al <sub>2</sub> O <sub>3</sub> , 4.0 SiO <sub>2</sub> .
19	0.3 K <sub>2</sub> O } 0.7 CaO } 3.5 Al <sub>2</sub> O <sub>3</sub> , 35 SiO <sub>2</sub>	Feldspar 83.55 Marble 35.00 Quartz 804.00 Zettlitz kaolin 414.40	
20	0.3 K <sub>2</sub> O } 0.7 CaO } 3.9 Al <sub>2</sub> O <sub>3</sub> , 39 SiO <sub>2</sub>	Feldspar 85.55 Marble 35.00 Quartz 900.00 Zettlitz kaolin 466.20	
21	0.3 K <sub>2</sub> O } 0.7 CaO } 4.4 Al <sub>2</sub> O <sub>3</sub> , 44 SiO <sub>2</sub>	Feldspar 83.55 Marble 35.00 Quartz 1020.00 Zettlitz kaolin 530.95	
22	0.3 K <sub>2</sub> O } 0.7 CaO } 4.9 Al <sub>2</sub> O <sub>3</sub> , 49 SiO <sub>2</sub>	Feldspar 83.55 Marble 35.00 Quartz 1140.00 Zettlitz kaolin 595.70	
23	0.3 K <sub>2</sub> O } 0.7 CaO } 5.4 Al <sub>2</sub> O <sub>3</sub> , 54 SiO <sub>2</sub>	Feldspar 83.55 Marble 35.00 Quartz 1260.00 Zettlitz kaolin 660.45	
24	0.3 K <sub>2</sub> O } 0.7 CaO } 6.0 Al <sub>2</sub> O <sub>3</sub> , 60 SiO <sub>2</sub>	Feldspar 83.55 Marble 35.00 Quartz 1404.00 Zettlitz kaolin 738.15	
25	0.3 K <sub>2</sub> O } 0.7 CaO } 6.6 Al <sub>2</sub> O <sub>3</sub> , 66 SiO <sub>2</sub>	Feldspar 83.55 Marble 35.00 Quartz 1548.00 Zettlitz kaolin 815.85	
26	0.3 K <sub>2</sub> O } 0.7 CaO } 7.2 Al <sub>2</sub> O <sub>3</sub> , 72 SiO <sub>2</sub>	Feldspar 83.55 Marble 35.00 Quartz 1692.00 Zettlitz kaolin 893.55	

No.	Chemical formula.	Mixture.	
27	0.3 K <sub>2</sub> O } 0.7 CaO } 20 Al <sub>2</sub> O <sub>3</sub> , 200 SiO <sub>2</sub>	Feldspar 83.55 Marble 35.00 Quartz 4764.00 Zettlitz kaolin 2551.13	
28	— Al <sub>2</sub> O <sub>3</sub> , 10 SiO <sub>2</sub>	Quartz 240.00 Zettlitz kaolin 129.50	
29	— Al <sub>2</sub> O <sub>3</sub> , 8 SiO <sub>2</sub>	Quartz 180.00 Zettlitz kaolin 129.50	
30	— Al <sub>2</sub> O <sub>3</sub> , 6 SiO <sub>2</sub>	Quartz 120.00 Zettlitz kaolin 129.50	
31	— Al <sub>2</sub> O <sub>3</sub> , 5 SiO <sub>2</sub>	Quartz 90.00 Zettlitz kaolin 129.50	
32	— Al <sub>2</sub> O <sub>3</sub> , 4 SiO <sub>2</sub>	Quartz 60.00 Zettlitz kaolin 129.50	
33	— Al <sub>2</sub> O <sub>3</sub> , 3 SiO <sub>2</sub>	Quartz 30.00 Zettlitz kaolin 129.50	
34	— Al <sub>2</sub> O <sub>3</sub> , 2.5 SiO <sub>2</sub>	Quartz 15.00 Zettlitz kaolin 129.50	
35	— Al <sub>2</sub> O <sub>3</sub> , 2 SiO <sub>2</sub>	Zettlitz kaolin	
36	— — —	Rackonitz shale-clay	

The melting of these tetrahedrons determines the temperatures between the melting-point of 90 gold, 10 platinum (that is, about 1145°) and the highest heat of the porcelain fire. The temperatures which correspond to the melting-points of the cones 21 to 26 are reached in the iron and water gas industries. The cones 26 to 36 serve for the determination of the refractoriness of clays.<sup>1</sup>

<sup>1</sup> In connection with these cones 1 to 36 the publishers have later on made lower melting cones, 01-022, see *Thonindustrie Zeitung*, 1892 and 1895, of which the numbers 01-010 go down to silver melting heat and are used for the burning of easily fusible brick clays, while the numbers 011-022 descend to dark red heat and are intended for the fixing of colors, enamels, and gold decoration in muffles.

It has also been endeavored to compound the glazes in such a manner that only their silica content is increased, the alkali and lime, as well as the alumina content, being always the same. The glazes would thus have the composition :



But in these, in the higher numbers, there appeared devitrification phenomena, owing to the continued decrease of the basic constituents, while those in which an increase in alumina is simultaneous with the rise in silica, up to the most infusible ones, do not show these peculiarities, but always result in smooth non-crystalline mixtures.

I want to state that the temperature differences, which mark the melting-points, are not constant; this can be determined in a sufficiently accurate manner by observing the cones in the kiln. The cones 1, 2, 3, 4, were melted down in the test-kiln in quite uniform intervals of time; their melting-points lie consecutively between the platinum gold alloys 90 gold, 10 platinum, and 80 gold, 20 platinum; ordinarily they went down in intervals of from ten to fifteen minutes. Then followed 5, 6, and 7, which do not vary much in regard to melting-point, and were melted down in intervals of about five minutes. Then again there appeared quite a regular interval between the remaining cones which was estimated to be in the average from one-quarter to one-half hour with the higher numbers. But I did not desire to do away with the cones 5, 6, and 7, because their numbers correspond to the acidity. There is to be considered that the cones of the higher numbers always are slower to fuse; this can be explained by the fact that at higher temperatures, on account of the continually increasing heat losses the temperature of the kiln always rises more slowly, and also the glazes become more viscous and for this reason go down more reluctantly.

When using cones one must always bear in mind, when placing them, that they always bend towards one and the same side; and that is the open side of the mold, on which the cone is stamped with the number. They are also to be set, so that the going down of the point can be observed. The instant at which

the point of the bending cone touches the fire-clay tile serving as the support is best to be considered as the beginning of fusion.

Since the kilns of the ceramic industry always show differences in regard to temperature which is highest near the inlet of the fire and lowest at the outlet, the temperature must not be determined once at one place and then again at another, for this would practically lead to no result. It should rather be insisted that the temperature is always determined at the same place in the kiln.

All claywares require a minimum temperature in order to produce in the body or the glaze the finished condition; however, they must not be carried beyond a certain limit if disadvantages are not to result. The temperatures must, therefore, be measured at least at two places in the kiln where the highest and lowest temperatures prevail. The temperature measured by means of the cone, registers in one place the maximum which must not be passed, in the other place the minimum which must absolutely be attained. The places where the maximum and minimum are found will be now above, now below, now in front of the fire end, and again behind it, according to the construction of the kiln. Which place is chosen for the measurement of temperature, each one will have to determine for himself, according to the construction and the size of the kiln; the main point is that the trial cones be set at the same place in the kiln.

The trial cones must always be so placed that they can be observed through a horizontal tube. With the horizontal position of the tube, it may be closed by a disk of glass in the outer opening. It is not necessary to use a sheet of mica in this position; a perpendicular tube must, however, always be closed by a sheet of mica, because the glass invariably cracks in this case. Moreover, perpendicular tubes are easily covered with soot which seldom or rarely occurs with horizontal tubes, and if it does occur, the glass plate can easily be loosened and the soot removed. The tubes are either walled into the door or special channels are left in the kiln wall in building the kiln, or a hole is drilled through the kiln wall by means of an iron gas-pipe.

The cones must not stand too deep in the kiln because they

are then hard to see from without. When saggers are used in burning, the cones are placed into a sagger, open at both ends. Where this is not the case, a special flue or channel must be constructed to make them visible. The cones are seen much more readily if this channel is extended some distance beyond them.

The cones always incline to the same side, that side on which the number is imprinted generally becoming the top side. To protect them from falling over when they begin to bend, they are fastened to a fire-clay tile. They are unburned and made hard by an addition of mucilage. If they are moistened at the bottom, and rubbed somewhat on a moistened fire-clay tile, they will firmly unite with the latter in drying, and are prevented from falling in the kiln.

The cones are considered melted when the bending point touches the fire-clay tile; this instant is always to be noted carefully, and when the cone is correctly placed can be observed accurately.

In order to determine what cones are required for a good burn, it is necessary to set a whole series of cones in the kiln the first time, so as to note to what cone fusion takes place, observing the temperature according to the old method; for the maximum and minimum temperature the number of the cones can be easily found. When this has once been determined it is only necessary to insert one, or at most, two consecutive numbers.

Thus, for example, I burned the Seger porcelain always with only three cones: at the place where the fire enters, with Nos. 9 and 10, at the outlet with No. 8. The cone No. 8 must have gone down if the burn is to be finished; that cone No. 10 should likewise go down is not necessary, since it represents the maximum temperature.

The temperatures which are used in practice vary exceedingly according to the material which is used and the purpose of the burning; in general, however, there are used: For easily fusible clays containing lime and iron, for clinkers, floor tiles and similar products, cones up to No. 10; for stoneware with salt or slip glaze, cones No. 5 to No. 10; for white ware, in the

biscuit burn Nos. 3 to 10; in the glaze burn up to No. 5; for fire-clay ware, Nos. 10 to 20; for porcelain, Nos. 10 to 20; for the iron, glass and water-gas industries, cones up to No. 26; for the determination of the refractoriness of clays, cones from No. 26 to No. 36.



## **B. TREATISES WHICH RELATE TO SPECIAL BRANCHES OF THE CLAY INDUSTRY**

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### **I. ESSAYS REFERRING TO BRICK AND TERRA COTTA**

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#### **Theoretical Considerations of Drying in the Open Air and in Closed Dryers**

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**PROFESSOR EDWARD ORTON, JR., TRANSLATOR**

The question of drying plants by means of which it is possible to continue manufacturing even in winter without interruption, or at least without too heavy an expense, has ripened communications and discussions in regard to experiments towards this end on various sides. It cannot, however, be said that the problem has been solved even in a partially satisfactory manner. There have not only been constructed drying houses which are heated by kilns contained in them, that is, by the radiated heat and the heat escaping from the cooling chambers, but also such which are provided with special heating arrangements of different systems. Again, there have been constructed special, sometimes very ingenious, dryers which are based upon the idea to carry on the drying process continuously, as it is done in the burning of continuous kilns, whose operation is simultaneous with the working of the machine and the burning of the kiln.

For drying, as will be proved later on by calculation, a very large amount of heat is consumed, which is, so to speak, annihilated for the senses. This is true whether the drying proceeds in the open air or in the heated rooms, and however large this theoretically required amount of heat may be. Again, in drying, especially when it is carried out, as the material demands, at a comparatively low temperature, the movement of large

quantities of air is necessary in order to remove the water vapor formed. But the constructors of the different drying plants have hardly ever accounted for the various factors mentioned above, making but little use of the material offered by science. In most cases, after expensive experiments, they have arrived at the conclusion that the heating arrangements constructed, were capable of producing only a comparatively small part of the intended effect. Or, in places where the heating plant is so constructed that the generation of heat may be forced, it has often been found that the cost of the fuel used overbalances the advantage which accrues from the continuation of the manufacture during the cold season.

Only in cases where dryers have been constructed above periodic kilns which, after burning, give off a large amount of heat, stored in the walls and in the ware, is it possible to dry as much green ware by means of this waste heat as is necessary for maintaining the capacity of the works, and seemingly without cost. The attempt to solve the problem of operation in winter on the basis of this principle has not led to a solution, and the claim of drying without expense has really no foundation, since this is just as impossible as the production of power without expense; for in this way there is only obtained and made useful something which otherwise would uselessly go into the air, and this is accomplished in a somewhat crude manner; an amount of heat is used in an unsuitable way, which in an economically operating kiln would not need to be generated at all. Where special heating arrangements are constructed for winter drying actual results with artificial dryers have been obtained only where the cost of fuel is so low that a larger or smaller consumption does not change the cost of manufacture too much, or where other sources of heat are available for which, as waste heat, no account need be made.

Though the consumption of heat, in the construction of artificial dryers, or what is the same, their insufficient capacity, appeared to many unexpectedly, yet the large consumption of heat lies in the nature of the case. There has been a tendency, as is shown by the earlier debates on this subject in conventions, to

attribute this fact to the faulty construction of the drying plant and to look for a more perfect one. Hence the problem cannot be solved in all cases with a certain apparatus even the most perfect one, but in every special case the local conditions must be taken into account in order to decide the question whether artificial drying is advisable and economical at all, or whether it would not be more economical to make use beforehand of the sun's heat available during the summer time.

The laws of physics teach us that every fluid body, when it takes on the condition of a gas or vapor, requires a definite quantity of heat, which disappears to our senses and to the thermometer with the completion of this change of condition and which is called vapor heat or "latent" heat.

When, for instance, one heats water in a receptacle, the temperature increases steadily up to  $100^{\circ}$ , and then remains constant, while the water boils or the vapor rises up in bubbles. The steam generated also retains the same temperature.

The heat applied during the period of boiling is not able to raise the temperature of the water above  $100^{\circ}$ , but is used exclusively to change the condition of the water to a gas, and to the hiding of this necessary latent heat. In fact, the boiling ceases at once, when the heat is removed. The heat necessary for this transformation is now a perfectly well established quantity, determined in the case of the more important volatile liquids by researches of the greatest nicety.

Water alone is of interest to us in this connection and the quantity of latent heat, plus the measurable free heat of the boiling water, amounts to 610<sup>1</sup> heat units or calories, that is, a quantity of heat which is able to raise 610 kg. of water from  $0^{\circ}$  to  $1^{\circ}$  is needed to raise 1 kg. of water from  $0^{\circ}$  to steam. But the changing of water into vapor does not only take place at boiling temperatures, but at all lower ones as well; even ice vaporizes, but at all temperatures below  $100^{\circ}$ , the vapors do not rise in bubbles but are evolved slower from the surface of the liquid.

We call this slow vaporization, when a medium must be present to take up and remove the vapor as formed, evaporation.

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<sup>1</sup> [636 according to the latest researches.—Ed.]

In evaporation at low temperatures, however, as has been proved by researches with the most exact instruments, the same laws as to heat consumption hold good as in vaporizing, and though the quantities of heat established by science vary somewhat for different temperatures, still we can for all practical purposes call them equal. We use for all temperatures the number given above, 610 heat units, as the mean of the results found by many observers.

When water evaporates at  $0^{\circ}$ , it consumes as much heat as when it evaporates at  $100^{\circ}$ , that is, 610 heat units, and without the consumption of this heat, evaporation is impossible.

This unalterable relation between the evaporated water and heat units determines the fundamental law for the consideration of the drying process; but it is not the only factor coming into consideration. As described above, a medium is necessary for the occurrence of evaporation, which will carry away the water vapor as formed and permit the formation of new vapor.

This medium is air. Its ability to absorb water vapor is limited and depends on its temperature and on its tension or pressure; but since we find the last expressed by the barometer readings, almost constant, we are practically bound only by the former, or temperature.

If air can expand freely during its absorption of water vapor, it is able to take up at a given temperature such a quantity of water, that its tension, plus that arising from the water vapor taken up, is equal to the tension of the atmosphere as shown by the barometer.

The tension of water vapor has been determined from  $-30^{\circ}$  on, and there can now be calculated for any designated temperature and pressure, the maximum quantity of water the air can take up. In the following table by Prof. Magnus, the tensions of water vapor, in millimeters of a mercury column, are given for the temperatures which fall inside the limits of our consideration:

TABLE I

## TENSION OF AQUEOUS VAPOR ACCORDING TO PROF. MAGNUS

°C.	mm.	°C.	mm.	°C.	mm.
0	4.525	11	9.751	22	19.675
1	4.867	12	10.421	23	20.909
2	5.231	13	11.130	24	22.211
3	5.619	14	11.882	25	23.582
4	6.032	15	12.677	30	31.602
5	6.471	16	13.519	40	54.969
6	6.939	17	14.409	50	91.965
7	7.436	18	15.351	60	148.579
8	7.964	19	16.345	70	232.606
9	8.525	20	17.396	80	353.926
10	9.125	21	18.505	100	760.000

The quantity of water vapor which dry air can take up at any given temperature with an average tension of the atmosphere, that is, 760 mm. barometric reading, is equal to the tension given in the preceding table at this temperature divided by the tension of the air. For example, at 10° it is

$$\frac{9.125}{760} ; \text{ or at } 30^\circ, \frac{31.602}{760}$$

of its volume; the composition of the air saturated with moisture at 10° is 9.125 volumes of water vapor plus 760 - 9.125 = 750.875 volumes of dry air, and at 30° it is equal to 31.602 volumes of water vapor plus 728.398 volumes of dry air.

These examples will show any one how to calculate the carrying power of air for water vapor for any given temperature without difficulty.

If one wishes to calculate from these volumes the weight of water which any unit of air, for instance a cubic meter, can take up at any designated temperature the following formula, an explanation of which would carry me too far, will serve to give the results.

$$G = \frac{1,000,000S}{(1 + aT)} \cdot \frac{P}{b}$$

In this formula

- $G$  = the desired maximum weight of water vapor in grams in a cubic meter,  
 $S$  = the specific gravity of water vapor, at  $0^{\circ}$  C., and 760 mm. barometer. ( $= 0.000806$ , referred to water),  
 $t$  = temperature of air,  
 $a$  = coefficient of expansion of gaseous bodies  $= 0.003665$ ,  
 $\rho$  = tension of water vapor at the temperature  $t$  (see the preceding table, No. I),  
 $b$  = barometric reading.

Hence, the quantity of water which air at  $10^{\circ}$  and 760 mm. pressure, could take up would be:

$$\frac{1,000,000 \times 0.000806}{(1 + 0.003665 \times 10)} \times \frac{9.125}{760} = 9.3 \text{ grams},$$

or at  $30^{\circ}$  and 760 mm. barometric reading,

$$\frac{1,000,000 \times 0.000806}{(1 + 0.003665 \times 30)} \times \frac{31.602}{760} = 30.2 \text{ grams.}$$

For all practical purposes the barometer reading can be taken as constant, at 760 mm. and the maximum quantity of water, which can exist in a cubic meter of air, calculated by the preceding formula, is given in the following table, for the temperatures in question:

TABLE II

Temperature. °C.	Weight of water in grams per cubic meter of air. Grams.	Temperature. °C.	Weight of water in grams per cubic meter of air. Grams.
0	5.4	40	50.9
5	7.3	50	82.3
10	9.2	60	129.1
15	12.8	70	195.3
20	17.3	80	290.2
25	22.5	100	589.5
30	30.2		

When in any drying apparatus we know the quantity of water to be removed and the temperature of the air which is laden with moisture, the quantities of air escaping through the ventilating devices, be they chimneys or ventilators, or be it the

movement of air through the openings and due to the penetrability of the enclosing walls, could be directly calculated from this table, and the intermediate values interpolated with the help of the above formula, if the air, when it comes to us for use, were absolutely free from water vapor.

In fact this is never the case; although the atmospheric air seems entirely clear and transparent, it contains still considerable quantities of water vapor, since it stands everywhere in contact with water areas and with damp earth surfaces.

A clouding of the air is noticeable only when it has already taken up the maximum water content and has become useless for drying.

Therefore, if its capacity for drying is to be determined, the quantity of its water vapor must be considered. If air, which contains water without being completely saturated by it, is cooled down, a point is reached when the maximum water content is attained, since its power to hold water vapor becomes constantly less with a falling temperature, as is shown in the above table.

If the cooling proceeds below this point, a part of the water vapor must be separated out in the liquid state, and this happens according to the quantity of the separation and the temperature, as rain or snow, clouds, dew or frost. We call the temperature at which the air attains its point of saturation for water vapor, the dew-point.

Air which has reached this point of saturation is unfit to take up more water vapor, unless its capacity is again increased by heating. For this reason foggy air, which is always saturated, can not dry even with the strongest motion.

The quantity of water vapor which is present in the air and which influences more or less its ability to act as a drying agent, is dependent on climatic conditions, the greater or smaller distance from large bodies of water, the direction of the wind, temperature of earth and air, the season of the year, etc. The quantity of water vapor or its degree of humidity, is determined by the hygrometer, or for practical purposes, the psychrometer.

This simple instrument consists of two concordant ordinary

mercurial thermometers, which are fixed side by side to a small board. The globe of the one is closely wrapped with muslin, which is laced together over and under the same and which dips into a little vessel of water, so that the bulb is always kept moist. While the second thermometer indicates merely the temperature of the air, the former, with the constantly moistened bulb, from which evaporation is continually taking place, always is in contact with a saturated atmosphere and shows a temperature which lies very near to that at which the air is saturated with water vapor, that is, the dew-point. For instance, if the dry bulb shows the temperature of the air to be  $15^{\circ}$ , and the wet bulb shows the dew-point as being at  $10^{\circ}$ , we find the moisture content of the air as follows:

According to Table I, the maximum possible water vapor at  $15^{\circ}$  (and 760 mm. barometer) =  $\frac{12.677}{760}$  of the air volume. The water vapor actually present is only that amount which corresponds to the saturation at  $10^{\circ}$  =  $\frac{9.125}{760}$ . The relative ratio of the two thus is as  $12.677 : 9.125$  or  $100 : 72$ . We say the air contains 72 per cent of moisture, that is, 72 per cent of that quantity which it is able to absorb at the temperature observed. The absolute quantity of water which the air may still take up is calculated by the formula given above, or Table II, which has been deduced from it.

	Water vapor. Grams.
1 cubic meter of air at $15^{\circ}$ can take up a maximum of	<u>12.7</u>
According to the position of the dew-point ( $10^{\circ}$ ) it contains	<u>9.2</u>
Hence it is capable of still taking up, per cubic meter	<u>3.5</u>

The amount of water which the air contains and by which the further power of absorption of moisture is determined, is variable according to local conditions and the time of the year. As an average of the systematic and extensive observation of many years, the following has been determined for Halle, which shows the following relative humidity for the different months:

January	85.8	May	69.2	September	72.8
February	81.0	June	71.0	October	78.9
March	77.3	July	68.5	November	85.6
April	71.3	August	66.1	December	86.8

It is seen from this that in the summer months at most about one-third, and in the winter months about one-eighth, of that quantity of water can be absorbed by the atmospheric air, which could be taken up at the average temperature of the separate months, since over two-thirds and seven-eighths of the quantity of water is already present.

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After this introduction to the scientific foundation of the drying process, let us consider the latter under definite conditions whose values we can determine, taking up first the drying in the open air.

According to the investigations which have been carried on with brick materials by members of the Association, and which have been made with brick machines of the systems most widely distributed in Germany, such as the Schlickeysen, Sachsenberg, and Hertel, the moisture content of freshly molded bricks amounts on the average of twenty-five machines to 24.9 per cent of the dry weight of the clay.

Of the water content there remains in the clay in the form of hygroscopic water, which is not evaporated at ordinary temperatures, and which is only driven out at the somewhat higher temperatures of the water-smoking process in the kiln, in the same materials, an average of 3.4 per cent. There is, therefore, water to the amount of about  $22\frac{1}{2}$  per cent of the weight of the dried clay to be evaporated.

If we take the dry weight of 1000 unburnt bricks to be about 3500 kg., we can calculate that, from the 1000 bricks, there will be, on the average, about 788 kg. of water evaporated in order to obtain bone-dry brick.

The amount of heat which is absolutely necessary for this evaporation and without whose assistance no drying whatever could take place, amounts to 788 kg.  $\times$  610 H. U. (heat units) = 480,680 H. U. according to the preceding statements.

In order to produce this quantity of heat with fuel, since coal generates on the average about 7500 H. U. on combustion, there are required  $\frac{480,680}{7500} = 64$  kg., theoretically, and practically a considerably greater quantity of heat.

We must now inquire into the source of the heat units necessary for the evaporation of the water in the open air.

It will have struck every brickmaker, when he steps between the racks of a drying shed or into the storehouse in which the not wholly dried bricks are packed, that a very refreshing coolness meets him, but also that cool air is not met between the drying racks, if the bricks therein are already well air-dried.

It will also have occurred to him that a noticeable difference in temperature cannot be detected in rainy weather, by which the drying process is entirely stopped. In fact, a strongly marked cooling which damp bodies experience, is always a sign that evaporation is going forward actively, and it is known that by accelerating evaporation, even in summer, quite low temperatures may be produced. However, this is possible only up to a certain point, and this is determined by the dew-point of the air whose office it is to take up the water vapors. When this point is reached the air can in no case take up any more water vapor.

The intensity of evaporation, that is, the quantity of water vapor taken up by the air, stands in a definite, unchangeable relation to the decrease in temperature experienced by it so that an equivalent can be determined between the loss of heat which it suffers and the quantity of water which is taken up.

Since a continual change of air between the inside of the drying plant and the outside air takes place, it is clear that the heat which the air loses in the drying racks, is to be regarded as that source of heat which is consumed as latent heat for the evaporation of the water. It is, therefore, the air itself directly and the heat of the sun indirectly, which is the source of the heat, that is consumed as latent heat in drying. The average summer temperature in Berlin is  $17^{\circ}$ . The amount of heat, which 1 cubic meter of atmospheric air contains at  $17^{\circ}$ , is equal to 5.542 H. U., or for every degree the air is cooled, it loses  $\frac{5.54}{17} = 0.326$  H. U.

If G, the weight of a cubic meter of air at  $0^{\circ}$  and 760 mm. pressure, = 1.299 kg., w, the specific heat of air, = 0.2669,

$t$ , the temperature of the air, and  $\alpha$ , the coefficient of expansion of air = 0.003665, then the quantity of heat

$$W = \frac{G \times w \times t}{(1 + \alpha t)} = \frac{1.299 \times 0.2669 \times 17}{(1 + 0.003665 \times 17)} = 5542 \text{ H. U.}$$

With a quantity of heat of 0.326 H. U. it is possible to evaporate  $\frac{1000 \times 0.326}{610}$  gram = 0.534 gram of water. Hence, for every degree centigrade which a cubic meter of air is cooled on passing through the dryer, a weight of 0.534 gram of water is the equivalent; that is, when 0.534 gram of water is changed to vapor a cubic meter of air, which takes up this steam and carries it away, loses 1° in temperature.

The quantity of heat, which is carried to the bricks of a drying plant by the circulation of air, is dependent, on the one hand, on the temperature and on the relative water content of the air, and on the other hand, on the velocity of the air current. It is dependent on the first, because the air is so much the more inclined to transfer its heat to water vapor, the farther it is removed from the point of saturation, that is, the farther its temperature is removed from that of the dew-point; on the second, because the air, as the source of heat, gives up the necessary quantity of heat with increasing rapidity as the air current increases in velocity.

Let us, in order to show the quantities of air which are necessary in drying in the open air under varying conditions of humidity, take the air temperature to be 17°, the dew-point at 10°, and the air current to have such a velocity that it is not allowed to lose all of the available 7°, but that by its movements through the drying racks it gives up only 3° of its temperature. Every cubic meter will then take up for these 3° which it has lost, a water content of  $3 \times 0.534 = 1.602$  grams. Since the quantity of water to be evaporated, according to our previous assumption, is equal to 788 kg. = 788000 grams per 1000 bricks, then for every thousand bricks which are in the racks  $\frac{788000}{1.602} = 491885$  cubic meters of air must be carried through by the draft.

If the air at this temperature (17°) were, however, near

its point of saturation, with its dew-point, for example, at  $16^{\circ}$ , and the air without reaching this point could in consequence cool off only about  $0.5^{\circ}$ , the quantity of air necessary for giving up the heat and taking up the moisture would be sixfold.

It is said that for brick-drying, hot weather is very desirable, but that in windy weather, the drying also takes place rapidly at lower temperatures.

This is perfectly true, though only in so far as the air is not wholly saturated with moisture, and hence is not entirely unfit to take up more water vapor, unless it is itself first heated considerably.

A mechanical removal of particles of water, which are not transformed into vapor by the moving air, a view which has been brought out repeatedly before the Association, is neither scientifically possible nor borne out by the facts.

Whether the air is originally at  $17^{\circ}$  or only at  $10^{\circ}$ , is immaterial for the drying, if the dew-point lies so far below this temperature that the air in every case can give up an equal quantity of heat, without reaching the point of saturation by this cooling.

Since the quantity of heat, which the air receives from the inexhaustible source of the sun and which it can give up for evaporation according to the proportion of the possible and the actually present moisture at the temperature given, is always a small amount, and since the loss of heat is scarcely noticeable to the senses and under the most favorable circumstances does not amount to more than a few degrees, therefore the quantity of air required on drying in the open air is under all conditions very large and the prime mover of the drying process in open air is to be found in the *rapidity of the circulation*.

But the conditions are somewhat different in drying in closed chambers. Here the exclusive source of the heat consumed by the process of evaporation is not the air brought in, but is some artificial source, and to the heat consumption, which is required to replace the heat becoming latent, there must be added another, due to the fact that not only the air laden with moisture, but also the dried bricks, possess a higher temperature than the air and bricks which are conveyed into the drying chamber.

If we take, for example, the moisture-laden air of a drying chamber, which is removed by some method of ventilation at a temperature of  $20^{\circ}$ , while it enters at a temperature of  $4.5^{\circ}$  (the average temperature of the six winter and spring months at Berlin), the quantity of heat which is taken out by the air, without being used in the drying itself, can be calculated to be 4.89 heat units for every cubic meter, and the quantity of heat which is necessary to heat up 1000 bricks also from  $4.5^{\circ}$  C. to  $20^{\circ}$ , to be 11850 heat units.

A cubic meter of air at  $20^{\circ}$  contains, when saturated with water vapor at 760 mm. barometric pressure (Table I),  $\frac{17.396}{760}$  water vapor, and  $\frac{760 - 17.396}{760} = \frac{742.604}{760} = 0.974$  cubic meter of dry air.

The quantity of heat according to the formula:

$$w = \frac{G \times w \times t}{(1 + at)} \text{ for 1 cubic meter of dry air, or}$$

$$w_i = \frac{G \times w \times t}{(1 + at)} \times 0.974 \text{ for 1 cubic meter of moist air at } 20^{\circ}, \text{ or} \\ = \frac{1.299 \times 0.2669 \times 20}{(1 + 0.003665 \times 20)} \times 0.974 = 631 \text{ heat units.}$$

The above 0.974 cubic meter of air at  $20^{\circ}$ , on entering the dryer at an atmospheric temperature of  $4.5^{\circ}$ , that is, with a temperature difference of  $15.5^{\circ}$ , has occupied a volume of  $\frac{0.974}{(1 + 0.003665 \times 15.5)} = 0.914$  cubic meter, or saturated with vapor at  $4.5^{\circ}$ :

$$0.914 \times \frac{760}{760 - 6.25} = \frac{0.914}{0.991} = 0.922 \text{ cubic meter.}$$

The heat capacity of this amount of air at  $4.5^{\circ}$  is

$$\frac{1.299 \times 0.2669 \times 4.5}{(1 + 0.003665 \times 4.5)} \times 0.922 = 1.42 \text{ heat units.}$$

The difference of the two,  $6.31 - 1.42$ , gives the heat carried out of the dryer at  $20^{\circ} = 4.89$  heat units.

If 3500 kg. is the weight of 1000 bricks, 0.2 the specific heat of the clay and  $15.5^{\circ}$  the temperature difference, then the quantity of heat is  $35000 \times 0.2 \times 15.5^{\circ} = 11850$  heat units.

Although the absolute quantity of moisture, which the air

contains in winter, when artificial drying has its only application, is considerably less than in the summer, and the former becomes, after being heated, much more able to absorb water vapor than that which is present at the same temperature in the summer; still the quantity of air is, in this case, a very large one, although it does not become equal to that necessary for drying in the open air.

If we assume that in winter and spring in artificial drying plants the air is taken in at an average temperature of  $4.5^{\circ}$ , and that its content of moisture amounts, in the average of the observations, to 80 per cent, then the quantity of water which 1 cubic meter already contains is  $6.25 \times 0.80 = 5.00$  grams. (Calculated from Table I.) The same air heated to  $10^{\circ}$ , by which it expands, would contain in 1 cubic meter 4.9 grams, at  $20^{\circ}$ , 4.7 grams, at  $30^{\circ}$ , 4.5 grams, and at  $40^{\circ}$ , 4.4 grams of moisture.

The volume of air after being heated is calculated from the formula

$$v' = v \times (1 + \alpha [t - t_0]),$$

in which

$v$  = the original volume,

$v'$  = the volume after expansion,

$\alpha$  = the coefficient of expansion = 0.003665,

$t - t_0$  = the temperature difference.

Since the quantity of moisture remains unchanged, it decreases, referred to the cubic meter, in the measure in which the volume increases on expansion; there is thus obtained :

$$G_1 = \frac{G}{1 + \alpha (t - t_0)}$$

in which  $G$  = the weight of water before expansion and  $G_1$  = the weight of water after expansion.

On deducting the above quantities of moisture from those which 1 cubic meter of air can contain as a maximum at the designated temperature (see Table I), there is obtained the quantity of water which the air has abstracted from the drying brick, assuming that the air when conducted from the drying apparatus is fully saturated with moisture, and this amounts to :

TABLE III

At 10° =	9.2 - 4.9 =	4.3 grams,
At 20° =	17.3 - 4.7 =	12.6 grams,
At 30° =	30.2 - 4.5 =	25.7 grams,
At 40° =	50.9 - 4.4 =	46.5 grams,
At 50° =	82.3 - 4.2 =	78.1 grams,
At 60° =	129.1 - 4.1 =	125.0 grams,
At 70° =	195.3 - 3.9 =	191.4 grams,
At 80° =	290.2 - 3.8 =	286.4 grams,

for every cubic meter of moist air.

Now in order to take up and carry away in the form of vapor in the air the water content of 1000 bricks, amounting to 788 kg. or 788000 grams, there would be necessary:

At 10°, $\frac{788000}{4.3}$ =	183256 cubic meters.
At 20°, $\frac{788000}{12.6}$ =	60952 cubic meters.
At 30°, $\frac{788000}{25.7}$ =	30661 cubic meters.
At 40°, $\frac{788000}{46.5}$ =	16946 cubic meters.
At 50°, $\frac{788000}{78.1}$ =	10090 cubic meters.
At 60°, $\frac{788000}{125.0}$ =	6304 cubic meters.
At 70°, $\frac{788000}{191.4}$ =	4117 cubic meters.
At 80°, $\frac{788000}{286.4}$ =	2751 cubic meters.

It is seen that the volume of air which is able to carry out the water vapor from a drying plant, decreases very rapidly with the increase of temperature, but that it remains a considerable quantity even at moderately high temperatures.

As has already been stated, the heat in artificial dryers is not wholly confined to the heat consumption due to the change of state of water (latent heat, that which is used up in the evaporation of the water) but that another consumption of heat is tied up with it, from the fact that the air laden with moisture must be taken out at a higher temperature than it possessed be-

fore, and also that the dried bricks themselves assume the same temperature.

If we take these factors into consideration, then, for example, the total consumption of heat, if the moist air is carried out at  $20^{\circ}$ , is as follows:

As calculated, the quantity of heat which 1 cubic meter of air takes up when heated from  $4.5^{\circ}$  to  $20^{\circ}$ , amounts to 4.89 heat units. At this temperature, as above shown, the volume of air necessary for the absorption and carrying off of the water vapor from 1000 bricks (788 kg.) is 60952 cubic meters; the heat carried off by this quantity of air amounts to  $60952 \times 4.80 = 298055$  heat units. The latent heat of 788 kg. water vapor amounts to  $788 \times 610 = 480680$  heat units.

The heat required for warming the clay is  $\frac{11.850}{790.585}$  heat units corresponding together to a total consumption of  $\frac{790.585}{7500} = 105$  kg. of coal (in round numbers) per 1000 bricks.

In practice in consequence of the unavoidable losses of heat this theoretical consumption of coal is largely exceeded.

It is seen that the consumption of coal in itself is not so great that on this account the construction of drying plants should not be feasible, provided that in the construction of the same, sufficient care is taken that the losses of heat are reduced as much as possible.

This, however, is always very difficult; but it seems still more difficult to produce the flow of air which is needed, as deduced from the preceding calculations in order to carry out the water vapors formed at comparatively low temperatures.

In drying in the open air the wind does this sufficiently, but in closed chambers this condition does not exist, and the air must be supplied by some ventilating device such as a chimney or blower, and it seems that this is the sore point of the winter drying apparatus constructed so far.

If one expects to be able to produce the required ventilation simply through openings in the roof of the drying chamber, through which the large quantities of air can escape, he will run in danger of allowing a great quantity of air to escape, which

has not yet been saturated with moisture; such a ventilating device will be influenced by the circulation of air on the outside in a very disturbing manner. One can depend on being able to dry large quantities of ware in such a room only when very considerable quantities of heat, otherwise unused, are at his service as is the case, for example, when the dryer is located over a periodic kiln or a Mendheim gas kiln.

Where, however, separate heating devices must be applied for supplying heat to the dryer, a controllable means of ventilation must be provided, if one does not wish to run the danger of consuming excessive quantities of coal.

If we compare the air volumes found above, with those, which a continuous kiln would use for the burning of a similar quantity of brick, in order to obtain a basis as to what may be expected of the ventilation produced by a chimney, it will be seen that only about 3100 cubic meters of air at 40° are required, assuming that for the burning 200 kg. of coal are used, that a quantity of air double the theoretical amount needed in burning, is admitted to the fire, and that the products of combustion reach the stack at a temperature of 40°. It thus becomes evident that the quantity of air which is required for drying is very much greater than that necessary for burning an equal quantity of brick, and that the quantity of air to be moved through the chimney in burning amounts to only  $\frac{1}{5}$  of the air needed at a drying temperature of 40°,  $\frac{1}{10}$  at 30°,  $\frac{1}{20}$  at 20°, and only decreases so that it corresponds to the delivering capacity of a chimney of not excessive dimensions between the temperatures of 70° and 80°.

In order to make clear the meaning of the accompanying table of the theoretical quantities of air necessary for drying, let us assume a plant, in which 5000 full sized bricks are daily burned in a continuous kiln; for such a plant, as has been sufficiently proved by practice, a chimney would be used, for obtaining draft, of a height of 25 meters and with a clear opening of 0.8 meter at the top. There would also have to be erected a chimney for the drying plant, with a capacity corresponding to that of the kiln, 5000 bricks per day, whose purpose would be to venti-

late the drying chamber. The drying plant is assumed to be the most perfect of which we can conceive, and the quantity of air and coal used in it are assumed to be equal to the theoretical consumption.

If now we calculate the capacity of such a chimney<sup>1</sup> we will find, that it can carry off the following volumes of air:

Outside temperature 4.5°.

Inside temperature. °C.	Per minute. Cubic meters.	Per day (24 hours). Cubic meters.
20	30.5	43920
30	38.4	55440
40	45.9	66096
50	52.3	75212
60	59.6	85824
70	64.8	93312
80	69.55	100080

The two tables dealing with the quantities of air which are necessary at different temperatures in order to take up and carry out the water vapors which are set free as well as that which gives the capacity of a chimney, are most important for our consideration. They show that one can expect to remove only the quantities of water vapor by means of a chimney when the drying is carried on at a tolerably high temperature with a minimum of 40°; chimneys of very abnormal dimensions would be required for lower temperatures, or one would be compelled to make use of an exhauster, which again corresponds to a considerable expense for power and heat, so that in this way the eco-

<sup>1</sup> That is, if

$t - t_1$  = the temperature difference between the shaft of the chimney and the outside air,

$d$  = diameter of the chimney at its mouth,

$h$  = the height,

then the products of combustion will flow from the chimney with a velocity of

$$V = 628 \sqrt{\frac{(t-t_1) dh}{4.08 + 0.016 h}} \text{ meters per minute,}$$

and the quantity of air per minute amounts to

$$V = \frac{\pi d^2}{4} \times v = \frac{\pi d^2 \times 628}{4} \times \sqrt{\frac{(t-t_1) \times dh}{4.08 d + 0.016 h}},$$

or in twenty-four hours

$$\frac{\pi d^2 \times 6.28 \times 24 \times 60}{4} \times \sqrt{\frac{(t-t_1) dh}{4.08 d + 0.016 h}}.$$

nomic efficiency of winter drying appliances would be destroyed.

In any case, it is seen from the tables that the artificial drying appliances will be the better suited to attain a well-balanced capacity coordinate with the other manipulations of a factory, and that these results will be the more easily achieved, the higher the temperature that can be reached in them, and the warmer the air, laden with moisture, can be removed from them, because the difficulties of bringing about a suitable ventilation decrease with the elevation of the temperature.

And not only is the quantity of air which is to be moved less, but also the consumption of heat is less, the warmer the moist air can be drawn from the dryer. This sounds like a paradox, but it is nevertheless completely proved to be true. The relative quantity of heat which the air carries out is, of course, always greater at higher temperatures, since it increases proportionately with the temperature, but the absolute quantity of heat in the air is considerably greater at lower temperatures, because the volumes of air required increase in a very rapidly rising ratio with a decrease in temperature.

To be sure, unintentional losses of heat, which so far have been left out of our consideration, increase with a higher temperature in the drying apparatus; still it seems that the replacement of lost heat is much easier in practice than the operation with insufficient ventilation.

Drying at low temperatures, not exceeding  $30^{\circ}$  at the highest, will always demand large dimensions of the drying room, which usually ought to be used for other working purposes. Strange as it may seem, in the practical construction of such plants, no consideration has been bestowed upon the ventilation, in spite of the fact that theory insists on the most extensive use of ventilation, and it is left generally to the porosity of the walls and to unavoidable leaks to supply a very small part of the necessary change of air. It is even customary to prevent the penetration of every cold draft, because it is feared that the little heat evolved may be lost; this heat scarcely suffices to maintain a somewhat endurable temperature of the air, but does not suffice, by far, to furnish the heat for the evaporation of any considerable quantity of water.

One should never forget that the theoretical consumption of heat, which for ordinary conditions is to be considered as the minimum consumption of fuel, amounts to two-thirds of that which suffices in a well constructed continuous kiln for the complete burning of the ware, and that the actual amounts used will in most cases either equal or exceed this amount.

The heating of the drying chamber must therefore be carried so high, that, in spite of the strong ventilation, a very noticeable heating of the air will take place, if a winter drying plant is to dry a quantity of brick worth mentioning; and where this heat consumption, combined with the necessary air circulation, is not present, the capacity will always be small. In fact, in the majority of winter drying plants it can be observed that the brick, placed in the artificially heated dryers, furnish only a very small part of the dry ware which is required by a continuous kiln in regular operation.

Drying plants, which permit of working with higher temperatures, never exceeding 100°, however much they have met with scientific approval, have so far been exploited but very little and have for the first time demanded the attention of the public only during the last few years. Concerning the results of the constructions of this class, due to Weigelin, Ruehne and Bock, little or nothing is known at this time.

The drying at a high temperature will naturally always lead to compact apparatus and shorter time of drying, that is, a more rapid drying, and in this connection the question will always demand consideration as to whether the nature of the brick material permits rapid drying. Possibly the difficulties in this respect are greater than is generally believed.

The construction of drying plants is at this time a somewhat strongly cultivated field, but it can not be claimed that the majority of the systems carried out indicate that the constructors are fully cognizant of the natural laws which are to be considered, and that they have given them due consideration.

The preceding considerations are intended, without criticizing any of the different systems in use, only to test the plants already in existence as to their value, and in new plants to

furnish the data, which are fundamental for the heating and ventilating devices.

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### The Bock Tunnel Kiln

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W. H. ZIMMER, PH.D., TRANSLATOR

It is the purpose of all artificial drying arrangements to make the brick industry, as well as all other industries requiring extensive drying operations, independent of the slow method of drying in the air with the help of the sun's heat, replacing it by an artificial but more energetic source of heat. In this way the difficulties offered by a change in the temperature and humidity of the air or unfavorable climatic conditions are removed.

Supposing that there is an apparatus which is capable of removing the water to be evaporated in drying with the smallest possible quantity of fuel required, there remains the question to be answered: Can artificial and rapid drying be so carried on under these most favorable conditions, that it will adapt itself to the peculiarities of the material and the requirements of the entire manufacture?

This question, when dealing with clay, cannot be answered with an unconditional 'yes'.

In an earlier chapter I have treated the drying in open air and in closed spaces, and have developed in a purely theoretical manner the requirements which must be complied with by artificial dryers if the drying is to take place with such a consumption of fuel that the artificial process may compete successfully with the irregular but expenseless source of heat, the sun. Up to the present the brick industry does not possess such a dryer. I have proved in the essay referred to that the most favorable conditions for artificial drying are produced when it takes place as rapidly as possible, that is, at as high a temperature as possible and with a rapid change of air. But these requirements are so directly opposed to the properties of most ma-

terials used in the clay industry that the one prominent point of view appearing in connection with this dryer, drying with the minimum consumption of heat, cannot be considered the only determining one.

If artificial drying is thus required to be a rapid process—and all constructions which have so far appeared depend upon rapid drying, since only through this can the artificial method compete with drying in the open air—still it is in contradiction, as a whole, to the nature of clay and the brickmaker knows only too well from experience that too rapid drying by the sun's heat and strong wind, is liable to do more damage than frost, against which a well arranged artificial dryer is, of course, ample protection.

For this reason, the attempt to simplify the manufacture of brick by accomplishing the drying by artificial means in one or two days, which in the open air under the most favorable circumstances requires fourteen days, but mostly much longer and, at least with most clays, cannot be shortened without injury to the ware, seems unjustifiable to me. There may be materials here and there which can be subjected to this treatment without special injury, but these are rare cases, and as a rule, the impossibility of such a shortening of time will be realized only too soon.

In regard to the shape of the Bock dryer there may be said that externally it corresponds to that of the tunnel kiln and many of the details are borrowed from the latter, although the interior arrangement corresponding to the purpose of the apparatus shows several essential differences. The dryer consists of a long straight tunnel, oblong in section, which, as in the tunnel kiln, serves for the reception of a train of cars, each of the latter being provided with racks for hacking the brick to be dried. The cars, loaded with fresh brick from the machine, are pushed into the tunnel at the stack end, as with the tunnel kiln, and are removed at the opposite end with the dried brick. The movement of the cars is accomplished by any power device which in this case need be less powerful than in the tunnel kiln since, owing to the low temperature, no sand troughs being required for separating the

wheels from the burning space proper, and since also lubrication is permissible. The floor of the drying tunnel consists of iron plates upon which rest the rails, and which at the same time form the covering of the heating flue constructed beneath the tunnel. The furnace, by means of which the dryer is heated, is located at the end opposite the stack end and consists of a grate furnace, adapted to the fuel used, or a gas generator. The furnace space is arched over with fire-brick for a short distance; after passing through this part the fire gases flow along beneath the iron plates mentioned, and after passing through the entire length of the dryer are drawn into the stack, the gases having been cooled down considerably. In this way the gases do not come in contact with the ware to be dried, but the heat generated is first given up to the iron plates forming the floor of the drying tunnel which transfer it to the brick by radiation. With this arrangement the temperature at the stack end of the dryer is, of course, the lowest, that is, at the place where the fresh bricks are introduced. The movement of the air which carries away the water vapors evolved from the brick in the tunnel is opposite in direction to the hot air flowing away from the fire. The former enters at the end of the tunnel at which the fresh bricks are carried in, taking the same direction as the train of cars, while the fire-gases used for heating flow beneath the iron plates of the floor in the opposite direction. It is thus made possible that the air in its course through the dryer may pass through continually warmer portions, thus preventing the water vapors taken up from being condensed again, and enabling the air, on moving through the higher temperatures, to take up and carry away successively a larger and larger quantity of water. When the air has reached the place where the temperature of the floor is the highest, that is, above the furnace, it has assumed the highest temperature and the maximum water content, and is then removed from the drying tunnel proper. For this purpose the ceiling of the tunnel is also covered with iron plates, and at some distance above an arch is built so that a flue is produced in the space between the two. This flue is connected, on the one hand, with the interior of the dryer at a

place above the furnace, on the other hand, with an iron pipe which is fastened in the stack concentric with the latter and independent of it. This flue carries the hot air, laden with water vapors, to the stack and gives it an opportunity to transfer its sensible, as well as a part of the latent, heat of the vapor, by condensation to water, to the iron plates forming the bottom of the flue and the ceiling of the drying tunnel, this heat being given off to the bricks by radiation from above.

The removal of any water condensed in this upper flue is accomplished by a slight inclination of the iron plates and a small exit pipe. The part of the water vapors not condensed and removed is carried up by the air into the stack. The drying tunnel extends beyond the furnace and the vent hole in the ceiling by being continued without the upper flue, so as to provide an opportunity for the cooling of the dried and hot bricks, before they are taken from the tunnel. The two ends of the tunnel are provided with doors for the taking in and removing of the cars which, as in the case of the tunnel kiln, takes place at short intervals. The door at the entrance end has an opening for the regulation of the inflow of air.

Although this arrangement must be considered as the one which corresponds best to the requirements of theory in regard to the most economic use of heat, more than any other artificial dryer constructed so far, yet the question arises whether it will be adopted even in only a few cases. From the practical standpoint, considering the material to be dried brick in this case, important objections may be raised. It appears as dangerous practice to shorten the time of drying considerably, especially with machine-made bricks which in general are more inclined to crack in rapid drying than hand-molded brick.

In most cases, if the dryer were to be introduced everywhere, which is the aim of the inventor, it might happen that not a single brick would leave it without being cracked. But this lies in the nature of clay. If clay is to dry without change of shape, that is, without cracking, the drying of the outer portions must not take place too rapidly. But this is possible only when the water passing away from the surface by evaporation is re-

placed from the interior by capillary attraction. This replacing process, however, requires a definite, and with some clays a considerable, length of time, and if this time is not allowed, a tension is produced on the surface by a greater contraction which is bound to lead to warping or breaking of the whole; although with some clays the balancing of the water from the interior to the surface is more rapid so that they are not injured by a more rapid drying than could be accomplished in the open air, and that hence this circumstance need not be considered in artificial drying, still there is danger from another source. The transfer of heat to the bricks to be dried is accomplished, both by direct radiation from the heated iron plates forming the floor and ceiling of the drying tunnel, and by the current of air which has been heated by the iron plates. Since the radiation of heat acts first upon the exterior of the brick set on the dryer cars, and since the circulation of the air is strongest along the walls of the dryer tunnel, beneath the ceiling and along the floor, because here the resistance due to friction is less than through the racks, the outside, and especially the upper and lower courses of brick, will be heated more rapidly than the interior ones, and a certain length of time will always be required in order to raise the brick of the interior to the temperature possessed by the outside ones. For the reason that the drying must take place comparatively rapidly if it is to be advantageous at all, the humidity of the air in the dryer must be very high, since the quantity of air which can be used for the removal of the water vapors is extremely small as compared with the quantity which is used in open-air drying. Hence, even the slight temperature differences of the surfaces of the outside and interior brick are liable to condense the water vapors, from time to time, which are evolved copiously near the iron heating plates, and will thus soften or crack the brick in the interior of the racks upon which condensation took place. Whether this difficulty can be removed in practice, whether or not other troubles will be met in actual operation, and again whether the iron heating plates offer sufficient radiating surface for conveying the quantity of heat required for drying to the body of the drying tun-

nel in a comparatively short time without raising the temperature too high, are all questions concerning which practical experience is still to be desired. We must wait till the latter is available; only then will it be possible to prove whether the dryer is of practical importance, no matter how plausible are the theoretical proofs of the advantages of the system. On the other hand, if practical experience has disclosed faults of construction it is not impossible that these may be overcome and that the dryer may be made a valuable adjunct of the clay industry.

The use of this dryer in the cement industry appears much more promising since it is founded upon such favorable theoretical principles. For this purpose the object is to dry bricks, low in clay, which contain less water, and also have a tendency to give off the latter more easily and more rapidly. Furthermore, it is not necessary that the brick should retain a strictly regular shape, and even when cracked here and there the pieces are still fit to be used in the process of manufacture. Such a dryer would perhaps prove especially useful in connection with dry presses which, of late, have become prominent in the cement industry.

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### Some Theoretical Considerations of the Water-Smoking Process in Continuous Kilns

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PROF. EDWARD ORTON, JR., TRANSLATOR

The last annual convention of the German Association for the Manufacture of Brick, Claywares, Lime and Cement, brought out a general and extended discussion of the water-smoking in continuous kilns. Not only were some communications made concerning the practical management of the water-smoking flues, which take the warm air, necessary for the water-smoking, out of the cooling compartments of the kiln, and transfer it to those newly set, and concerning various small portable furnaces, which were spoken of as being practical for the water-smoking in these

kilns, but there were made also certain allusions to new secret methods and new appliances for carrying on the water-smoking process in the continuous kiln in a safer and more economical manner.

These latter tend towards one end, namely, the separation of the water-smoking process not only from the real process of heating up and burning (which was recommended for continuous kilns many years ago, but unfortunately was carried out only in a few cases) but also the removal of the water vapor generated in water-smoking which is intended to be removed in the "most natural way," that is, by openings in the arches, in such a manner that the natural tendency of water vapor to rise might be made useful for its removal.

Even though it be true that the specific weight of water vapor is less than that of air under the same pressure and temperature, and, therefore, that water vapor generated in the atmosphere at atmospheric pressure (that is at 100°) rises, still one cannot speak of the natural tendency of water vapor to rise in the water-smoking process. Water vapors are evolved only with a simultaneous consumption of heat, which becomes latent, and in order to vaporize a given quantity of water a definite quantity of heat, capable of numerical expression, is required. Both the vapor formed and the heat consumed stand in an unalterable ratio. Since we must assume the air to be the carrier of the heat in the water-smoking process, be it heated in any way whatever, then in a unit volume at any readily established temperature it will contain a certain quantity of heat which can be used for the vaporization of liquid water. It is easy to establish how much water vapor can be formed by this quantity of heat and how much the air will be cooled off by this loss of heat. It is found here that the contraction of air through the loss of heat is much greater than the increase of volume which it experiences from the addition of water vapor formed by the heat which it has lost, and that therefore the air already used for water-smoking and thereby cooled, has become specifically heavier than the dry and warm air freshly introduced. If therefore, in practice, the air actually rises, this is not to be considered as a secret in-

nate tendency of its own, but must be ascribed to the fact that the heat, carried by the air, has been only partially used, and the air contained in the kiln is therefore warmer and lighter than that of the free atmosphere. Therefore, if any adjustment between the specifically lighter air on the inside of the kiln, and that of the outside takes place directly, then an upward movement will result in the kiln. But if an adjustment is effected with the still warmer air of the chimney of the continuous kiln, then the "natural way," which the air would take, would be from above to below. In the first case, the air must have retained a certain amount of heat, in the second the movement becomes the more pronounced, the more its heat is withdrawn and the greater the temperature difference between the air along the kiln floor and that in the chimney, whose draft is produced by some other source of heat. Just as in a vertical tube an upward current of air will be produced by heating the air column in comparison with the outside atmosphere, so a descending current will be produced by a cooling of the same; thus there arises an inverted chimney of the height of the kiln chamber to assist the operation of the kiln stack, if a stream of warm air is introduced under the arch during the water-smoking, its free heat being absorbed.

In no case, as long as the temperature of the water evaporating in the water-smoking compartment is below 100°, can a separation of the water vapor from the air in which the vapors were generated, take place; hence the water vapor has no opportunity to escape alone, nor in a greater degree, out of the upper openings of the kiln, than the air volume that is necessary to hold it in solution, which corresponds to the temperature governing the ability of the air to take up aqueous vapors. Investigations have shown that gases, which form in a space which is already filled with some other gas, are distributed according to the same laws as in vacuous space, that is, distribute themselves equally throughout the space; but this distribution, on account of the resistance which the gas already present exerts, goes on much slower than in the vacuum. If such a mixture is once made (and this must occur in water-smoking immediately on

vaporization, since every molecule of air must give up its heat to a water molecule in order to permit the vapor formation at all), a separation according to specific gravity can never occur later on, but the gases behave like two perfectly miscible liquids (like alcohol and water) but not like two non-miscible liquids (like oil and water). There can, therefore, be only a greater quantity of moisture in the air of the upper part of a kiln than in the lower, when the temperature of the air is higher on top, and hence its capacity for the absorption of water is greater; if the air is warmer below, there will be more moisture at the bottom.

Before I undertake to explain more precisely the phenomena which occur in water-smoking, and demonstrate numerically the modification of the same for various cases occurring in practice, I will come back to the nature of the water-smoking process, because I believe that many erroneous views are extant in reference to the subject.

Whoever has seen a clay analysis has observed that chemically combined water varying from 2 to 15 per cent with different raw materials, is always reported. This water cannot be removed by long-continued drying, but leaves only at a higher temperature; it is expelled only by ignition, and in most cases, its removal is shown by a change of color in the clay. In general the expulsion of the water is a chemical process and is accomplished by burning. When clay is mixed with water and reduced to a plastic condition, it will again lose, through evaporation, the largest part of this water. A part of the same, however, will be retained with great obstinacy in the pores of the clay and is not removed at the ordinary temperature of drying, but it requires heating to a point above the boiling-point of water or about 120° for its expulsion. Inversely clay which has been dried at 120°, when it is exposed to the atmosphere at ordinary temperatures, draws this quantity of water again from the air. This water, whose quantity varies between 1 and 8 per cent, is called hygroscopic water, and its expulsion, as well as of that which remains from insufficient drying, is accomplished in water-smoking. The water-smoking is finished, therefore, when all parts of the kiln chamber have attained a temperature lying a little above 100°.

For the removal of the hygroscopic water the introduction of a definite quantity of heat is necessary, which is absorbed in the change of water to steam. The introduction of this heat is always accomplished in practice by a current of heated air, whether from a special furnace provided for the purpose, or with air heated by the absorption of radiated heat from the cooling bricks by means of a water-smoking flue and chimney draft, or by the use of the still heated fire-gases moving away from the fire. From the economic standpoint, it would seem most suitable to use the last source of heat for this purpose, but we will see later on that the fire gases seem least suited of all to drive out the hygroscopic water at the temperatures at which it must be done.

The quantity of steam, which atmospheric air can take up, is a limited one, and is governed by the temperature of the same. The higher the temperature the greater the quantity of vapor the air can take up, till at  $100^{\circ}$  and above, the quantity of steam is independent of the quantity of air, hence from this point on, unlimited quantities of steam can be taken up. Since the water-smoking, as above explained, reaches its end at  $100^{\circ}$ , it becomes very necessary to investigate especially the capacity of the air to transport water at temperatures below  $100^{\circ}$ .

Water vaporizes at every temperature, at  $0^{\circ}$  as well as at  $100^{\circ}$ , but the tension with which the vapors are evolved varies considerably. The tension of the air is measured by means of the barometer. The tension of the atmospheric air is expressed by the height of a mercury column of an average length of 760 mm.; the tension of water vapor has been established by experiment for various temperatures. At  $100^{\circ}$  it is equal to that of air, or 760 mm., at  $50^{\circ}$  it amounts to 88.7 mm., at  $20^{\circ}$  to 17 mm., and at  $0^{\circ}$  to 5.1 mm.

The maximum quantity of vapor, which the air can take up at any given temperature, is a function of its tension, so that it contains at  $0^{\circ}$   $\frac{5.1}{760}$ , at  $20^{\circ}$   $\frac{17.3}{760}$ , at  $50^{\circ}$   $\frac{88.7}{760}$  of its volume of water vapor, and it is in condition to take up water vapor until this maximum is attained. If air contains less water vapor

than corresponds to the saturation of this temperature, and it is cooled, it will come finally to a temperature at which it cannot hold the water vapor already taken up; this point is called the dew-point of air; at this point a part of the water is deposited in the liquid state as dew.

The establishment of the dew-point is of the greatest importance for our consideration, because it indicates the temperature of the air at which it is still able to serve for drying and water-smoking, and below which it must never be cooled during the water-smoking process without incurring danger of spoiling the color of the ware to be burned, owing to condensation; this is especially true, when air which has been withdrawn from the fire is to be used for the water-smoking, since this already contains a large quantity of water, and carries with it other deleterious substances which are expelled from the clay when it is ignited.

While these particulars do not concern brick material of the lowest grades, in which in general only the form, hardness, and resistance to the weathering influences of the air come into consideration, where products of better quality are to be made, and where, therefore, beside the above-named properties, that of uniform color is necessarily demanded, the more or less correct operation of the water-smoking process forms a specially important factor in securing a faultless burn, and very great care must be used in this respect. It has been shown on earlier occasions that in all continuous kiln systems, of whatever construction, and fired with either solid fuel or gas, the conditions for the attainment of a uniform surface color are less favorable than in periodic kilns, because in the former the quantity of air, which carries away the water vapor of the green bricks, is limited. This is true, on the one hand, on account of the consideration for the most economic conditions of combustion, and on account of the smaller amount of fuel used; and on the other hand, because the fire-gases of a continuous kiln are less capable of taking up more water vapor on account of their high humidity than the air introduced from outside in the water-smoking process of a periodic kiln.

Superficial discoloration can be traced back in the majority

of cases to the deposits which are made on the surface of the cold bricks by the fire-gases, to the volatile ammonia and the alkaline salts, acid vapors, or flying particles of ashes which deposit with the water vapor, and which are left behind by the re-evaporation of the water, as salt efflorescence or ash deposits on the surface, or which alter the clay body chemically to a greater or less extent, and thus modify the color.

Phenomena which can be explained by the influence of the fire-gases on the bricks at the period of maximum heat, occur only in a few cases and only under unusual conditions. As to the assertion that color changes are produced by rapid or slower cooling of the brick, and which seems to be specially invented for illustrating the advantages of some particular systems, not a single scientific explanation has been attempted in proof of it. In the continuous kiln systems, and particularly in the ring kilns, it has been shown that discolorations, if they have not already arisen during the drying process owing to salt efflorescences, are avoided during the burning process by preventing the precipitation of water and with it other objectionable matter contained in the fire-gases.

The danger of brick becoming spoiled in the burning period of the ring kiln, that is, softened, cracked or discolored, is therefore the greater, the less the air, introduced for the purpose of water-smoking, is able to take up additional water and to carry it away quickly, and therefore, the more the air taken from the burning process is saturated with water vapor. The magnitude of this water content, if we do not consider the water vapors arising from a faulty isolation of kiln bottoms from the damp ground, is dependent on the water content of the fuel and its hydrogen content, on the chemically combined water of the clay which is expelled in burning, and on the amount of water which well-dried bricks still retain as the so-called hygroscopic water.

When we attempt to reduce the amount of water vapor in the fire-gases, we can do so up to a certain limit by the use of a fuel which has been dried, or which originally is low in water or hydrogen; in the brick material this cannot be altered, as the foundational supposition is the use of air-dried materials.

The following calculations will now serve to show the influence which the composition of the clay and the quantity of the fuel used for burning exerts on the composition of the fire-gases, and therefore, on the water-smoking process, and to illustrate the quantities of heat and air which are necessary in order to complete the water-smoking in every particular case.

### I. QUANTITY OF WATER VAPOR IN THE FIRE-GASES

The calculations are based on the use of three brick clays, free from lime, whose contents of chemically combined and hygroscopic water differ materially:

Sample.	Chemically combined water.	Hygroscopic wa- ter in terms of the dried clay.
From Schwarzehuette	2.5	2.6
From the Siegersdorf works	5.0	4.8
From the Greppin works	10.0	6.4

It is next assumed that all clays are used air dry, are burned with the same quantity of coal in a ring kiln, which amounts to 200 kg. of coal of average composition per 1000 bricks.

The coal is assumed to contain:

	Per cent.
Carbon	78.0
Hydrogen	5.2
Oxygen	11.8
Ash	5.0

Prof. Bischof gives as the average of sixty-seven kinds of coal, after deduction of the ash, 82.1 per cent carbon, 5.5 per cent hydrogen, 12.4 per cent oxygen, which, with the addition of 5 per cent ash, give the above figures.

If one assumes that the air carried to the fire amounts to just enough to burn the carbon to carbon dioxide and the hydrogen to water, then the following quantities of air would be required, since 6 parts by weight of carbon combine with 16 parts of oxygen, by weight, to form 22 parts of carbon dioxide and 1 part of hydrogen unites with 8 of oxygen to give 9 parts, by weight, of steam :

156 kg. of carbon unite with 416 kg. of oxygen and produce 572 kg. of carbon dioxide;

7.4 kg. of hydrogen unite with 59.2 kg. of oxygen and produce 66.6 kg. of steam.

The remaining 3 kg. of hydrogen unite with the 23.6 kg. of oxygen contained in the coal and furnishes 26.6 kg. of steam.

There will, therefore, be used 475.2 kg. of atmospheric oxygen; and since 1 cubic meter of oxygen at 0° and 760 mm. weighs 1.4323 kg., there will be 331.8 cubic meters of oxygen for 200 kg. of coal.

But there enters the burning chamber with the oxygen, its companion in the air, the nitrogen, and since for 100 parts by volume of air we have 21 per cent of oxygen and 79 per cent of nitrogen, the nitrogen will be 1248.2 cubic meters, and the air volume, which will suffice to just burn 200 kg. of coal of the above composition, will be  $331.8 + 1248.2 = 1580$  cubic meters.

Let us see what will be the constituent amounts of the products of combustion :

First, the nitrogen, which remains unchanged		1248.2 cu.m. N.
From the carbon there are produced, as shown above, 572 kg. of carbon dioxide which occupies the space of		288.6 cu.m. CO <sub>2</sub> .
From the elements of the water in the coal 26.3 kg. of steam are produced	32.2 cu.m.	
By combustion of the excess of hydrogen, 66.6 kg. of steam which is	82.7 cu.m.	
Thus together we have products of combustion to the volume of		115.9 cu.m. steam
		1652.7 cu.m.

The volumes are always reduced to standard conditions, that is, 0° and 760 mm. barometric pressure.

To these products of combustion there is now to be added the water vapor which arises from the expulsion of the chemically combined water from the clay in burning; this amounts, taking the weight of the burned bricks at 3 kg., to the following:

Clay from Schwarzenhuette (2.5 per cent) 75 kg. = 93.1 cubic meters.

Clay from Siegersdorf (5.0 per cent) 150 kg. = 186.2 cubic meters.

Clay from Greppin works (10.0 per cent) 300 kg. = 372.4 cubic meters.

The quantity and composition of the fire-gases, which arise through the burning of 200 kg. of coal, are thus equal to:

With chemically combined water.	2.5 per cent. Cubic meters.	5 per cent. Cubic meters.	10 per cent. Cubic meters.
Nitrogen - - -	1248.2	1248.2	1248.2
Carbon dioxide - - -	288.6	288.6	288.6
Water vapor - - -	209.0	302.1	488.3
Total - - -	1745.8	1838.9	2025.1

or expressed in per cent by volume :

	Per cent.	Per cent.	Per cent.
Nitrogen - - -	72.5	67.9	63.6
Carbon dioxide - - -	16.5	15.6	14.5
Water vapor - - -	12.0	16.5	21.9
Total - - -	100.0	100.0	100.0

We must now determine the dew-point for these combustion gases ; that is, to establish the temperature at which they are able to hold this water in the gaseous form and to carry it away. The tension of the air drawing off can be taken, without appreciable error, as being equal to the pressure of the outside atmosphere, that is, to the average barometric pressure of 760 mm. of mercury.

The rarefaction of the air in the flue of the lime ring kiln of F. Hoffman, at Nordhafen, in Berlin, amounted in several determinations to a maximum of 14.22 mm. of water pressure = 1.05 mm. of mercury. In this pressure the various constituents participate in direct proportion to their volumes. Hence the tension of the water vapors of the fire-gases is as follows, with the clay containing :

$$2.5 \text{ per cent combined water}, \frac{760 \times 12.0}{100} = 91.2 \text{ mm. mercury},$$

$$5 \text{ per cent combined water}, \frac{760 \times 16.5}{100} = 128.4 \text{ mm. mercury},$$

$$10 \text{ per cent combined water}, \frac{760 \times 21.9}{100} = 166.4 \text{ mm. mercury}.$$

The dew-point of the air coincides with that temperature at which water boils under a given pressure. We know from the researches of Dulong that the boiling-point of water corresponds to a tension

of 760.0 mm.	at	100°,
of 91.2 mm.	at	50°,
of 128.4 mm.	at	57°,
of 166.4 mm.	at	63°.

That is, translated into practical terms, as long as the bricks in the water-smoking compartments are heated to an average of 50° (with 2.5 per cent combined water), or 57° (with 5 per cent water), or 63° (with 10 per cent), according to the fundamental assumptions of this discussion, there can be no separation of water vapor from the fire-gases used for the water-smoking under any circumstances. On the other hand, wherever the temperature of the brick remains below the temperatures thus given, there will occur a precipitation of water.

If with the Greppin clay, the fire-gases were cooled down by contact with cold bricks to 50°, then there would be deposited from the quantity of fire-gases calculated for 1000 bricks, 206.9 kg., or nearly 7 per cent of the weight of the burned brick, of liquid water, since at 63° 389.9, but at 50° only 183 kg. of water vapor can be held in solution.

The separation of water must become smaller in proportion as the dew-point of the fire-gases is lowered because with the increasing temperature the power of the air to take up water vapor increases very rapidly, which is made evident by an inspection of the temperatures given above and the corresponding quantities of water held in solution.

In the preceding calculation the assumption was made, that only so much air was allowed to come to the fire as was just necessary for the combustion of the carbon and hydrogen to carbon dioxide and water. In practical work this proportion cannot be maintained, and Schinz states that only where gaseous fuel is used, where there is no obstacle to a rapid and complete mixture of fuel and air, is this at all practicable, while in the use of solid fuels, on account of the small superficial contact which it offers

to the atmospheric air, in the average, a quantity of air double the theoretical amount is needed in order to produce smokeless combustion. Unfortunately we possess no investigations in regard to the composition of fire-gases in continuous kilns, which might give us the required information, and a series of investigations, made with the Orsat apparatus for gas analysis, which Dr. Julius Aron described in the last convention of the German Clayware Manufacturers Association first inform us in regard to this point.

The statement of Schinz concerns only grate-firing, yet allows one to assume that the consumption of air in the continuous kiln lies between the two limits already mentioned, and we will, on that account, discuss, as the second extreme, those proportions which occur when the quantity of air which the chimney draws in for the combustion of the coal is twice as great as that theoretically necessary, or for 1000 bricks burned and 200 kg. of coal, there is used not 1582 but 3160 cubic meters of air.

In this case, the half of the air operates only as a dilutant, and the composition of the gases can be calculated as being :

With the clay containing	2.5 per cent. Cubic meters.	5 per cent. Cubic meters.	10 per cent. Cubic meters.
Nitrogen - - -	2496.8	2496.8	2496.8
Carbon dioxide - - -	288.6	288.6	288.6
Water vapor - - -	209.0	302.1	488.3
Oxygen - - -	331.8	331.8	331.8
Total - - -	3326.2	3419.3	3605.5

or expressed in per cent by volume :

	Per cent.	Per cent.	Per cent.
Nitrogen - - -	75.0	73.0	70.5
Carbon dioxide - - -	8.7	8.5	8.0
Water vapor - - -	6.3	8.8	12.3
Oxygen - - -	10.0	9.7	9.2
Total - - -	100.00	100.0	100.0

According to this, the tension of the water vapors and the dew-point are calculated to be as follows :

	Per cent chemically combined water.		
	2.5	5	10
Tension of vapor	47.9 mm.	66.9 mm.	93.5 mm.
Dew-point	38°	44°	51°

We will further investigate the influence that a greater or smaller supply of air to the fuel will have on the relative water content of the fire-gases and hence on the ability of the same to take up and carry away more or less water vapor during the water-smoking process, outside of the limits already expressed which correspond most closely to the conditions of actual work.

Let us assume that four times as much air is brought to the fuel as is necessary for theoretical combustion, which might easily happen in a badly managed plant. Then there would be required for the same quantity of coal (200 kg. for 1000 bricks),  $4 \times 1580 = 6320$  cubic meters of air.

Taking into account the water vapor arising from the clay during its dehydration, the products of combustion are :

For the clay containing	Per cent of chemically combined water.		
	2.5 (Schwarzehütte) Cubic meters.	5 (Siegersdorf) Cubic meters.	10 (Greppin) Cubic meters.
Nitrogen - - -	4993.6	4993.6	4993.6
Carbon dioxide - -	288.6	288.6	288.6
Water vapor - - -	209.0	302.1	488.3
Oxygen - - -	995.4	995.4	995.4
Total - - -	6486.6	6579.7	6765.9

The water vapor thus contained in the gases of combustion in per cent by volume is hence :

3.1 per cent                  4.6 per cent                  7.2 per cent  
of the fire gases, and the dew-points

26°

32°

41°.

If we assume, on the other hand, that the quantity of air introduced to the fuel is insufficient for complete combustion of the same to water and carbon dioxide, and for example is only sufficient to burn the hydrogen to water, and half of the carbon to carbon dioxide, while the other half of the carbon is changed to its lower form of oxidation or carbon monoxide<sup>1</sup> and is lost as such in the escaping fire-gases, then the composition of the gases will be as follows :

For clay with	Per cent of chemically combined water.		
	2.5 Cubic meters.	5 Cubic meters.	10. Cubic meters.
Nitrogen - - -	953.2	953.2	953.2
Carbon dioxide - - -	144.3	144.3	144.3
Water - - -	209.0	302.1	488.2
Carbon monoxide - - -	144.3	144.3	144.3
Total - - -	1450.8	1543.9	1730.0

The water vapor in this case amounts to

14.4 per cent

19.6 per cent

28.2 per cent

of the volume of the fire-gases, and the dew-point of the latter lies at

54°

61°

69°.

In all these cases, the absolute quantity of water vapor in the fire-gases remains the same, since the latter are composed of constant factors ; that is, the quantity of water which is formed by the burning of 200 kg. of coal, and that which is liberated by the dehydration of 1000 bricks. While the bulk of the other constituents varies both qualitatively and quantitatively, according to the amount of air admitted for combustion—insufficient, just enough, or excess.

For the purpose of drawing general conclusions for practical work from the preceding calculations, the same are once more summarized.

<sup>1</sup> While 6 parts by weight of carbon on burning to carbon dioxide unite with 16 parts of oxygen, on incomplete combustion, hence, with the formation of carbon monoxide they take up only one-half, or 8 parts by weight of oxygen.

Using 200 kg. of coal per 1000 bricks with clay containing :

	2.5 per cent chemically combined water. (Schwarzehuette).		5 per cent chemically combined water. (Siegersdorf).	
	Water vapor in per cent by volume.	Dew-point. °C.	Water vapor in per cent by volume.	Dew-point. °C.
With insufficient air (see above)	14.4	54	19.6	61
With sufficient air - - -	12.0	50	16.5	57
With double the required amount of air - - -	6.3	38	8.8	44
With four times the required amount of air - - -	3.1	26	4.6	32

	10 per cent chemically combined water. (Greppin).	
	Water vapor in per cent by volume.	Dew-point. °C.
With insufficient air (see above)	28.2	69
With sufficient air - - -	21.9	63
With double the required amount of air - - -	12.3	51
With four times the required amount of air - - -	7.2	41

From these figures, it is seen that, with the same clay and using the same quantity of fuel, the relative water content of the fire-gases is the greater, the smaller the quantity of air brought in for combustion, and with equal quantities of air used, it will be the greater, the higher the content of combined water in the clay. The dew-point rises in proportion to the per cent of the water content in the fire-gases.

This is important, because the dew-point is the lower limit at which the fire-gases can be used for water-smoking. If the entire kiln content possesses a higher temperature than the dew-point of the fire-gases, then these will be able to effect a removal of the water vapor. But if this temperature lies below the dew-point, then there must always occur an absorption of water by

the bricks, and this will exert a more or less injurious influence on the superficial color of the clay, according to the temperature and water content of the air, the kind and quantity of volatile salts or acid vapors in the fire-gases, and the greater or less porosity and the possible presence of soluble matter in the clays themselves.

The absolute quantity of the air alone, and its relative proportion to the fuel does not exert, as is set forth in the preceding remarks, a determinative influence upon the water content of the fire-gases, but the absolute quantity of the fuel used must be taken into consideration here, since it contributes to the formation of water and since the air required will also depend on its amount. The quantities of fuel which are used may vary within considerable limits, according to the hardness which it is desired to attain in the burning, and the temperature to which it is necessary to expose the ware in order to attain the purpose. If we modify the assumption made above that 200 kg. of coal are used in the burning, and assume on the one hand that the quantity is reduced to 100 kg. and on the other raised to 300 kg. per 1000 bricks, then the composition of the fire-gases would be as follows :

1a. Using 100 kg. of coal per 1000 bricks, and just air enough to consume it.

Clay with	Per cent of chemically combined water.		
	2.5 Cubic meters.	5. Cubic meters.	10. Cubic meters.
Nitrogen - - -	624.1	624.1	624.1
Carbon dioxide - - -	144.3	144.3	144.3
Water vapor - - -	151.0	244.1	430.3
Total - - -	919.4	1012.5	1198.7

The per cent of water vapor is accordingly,

16.4 per cent      24.1 per cent      35.9 per cent

and the dew-point of the fire-gases,

57°      65°      74°.

1b. Using twice the theoretical air supply, and 100 kg. of coal for 1000 bricks.

Clay with	Per cent of chemically combined water.		
	2.5 Cubic meters.	5 Cubic meters.	10. Cubic meters.
Nitrogen - - -	1248.2	1248.2	1248.2
Carbon dioxide - - -	144.3	144.3	144.3
Water vapor - - -	151.0	244.1	430.3
Oxygen - - -	165.9	165.9	165.9
Total - - -	1709.4	1802.7	1988.9

The per cent of water amounts to

8.8 per cent

13.5 per cent

21.6 per cent

and the dew-point is

44°

55°

63°.

2a. 300 kg. of coal per 1000 bricks, and just sufficient air to burn it.

Clay with	Per cent of chemically combined water.		
	2.5 Cubic meters.	5 Cubic meters.	10. Cubic meters.
Nitrogen - - -	1872.3	1872.3	1872.3
Carbon dioxide - - -	432.9	432.9	432.9
Water vapor - - -	266.9	360.0	546.0
Total - - -	2572.1	2665.2	2851.4

The fire-gases in this case contain of water vapor,

10.4 per cent;

13.9 per cent

19.1 per cent

and the dew-point is

48°

53°

60°.

2b. Using twice the required amount of air and 300 kg. of coal per 1000 bricks.

Clay with	Per cent of chemically combined water.		
	2.5 Cubic meters.	5 Cubic meters.	10. Cubic meters.
Nitrogen - - -	3744.6	3744.6	3744.6
Carbon dioxide - - -	432.9	432.9	432.9
Water vapor - - -	266.9	360.0	546.0
Oxygen - - -	497.2	497.2	497.2
Total - - -	4941.6	5034.7	5220.9

Percentage of water vapor in fire-gases :

5.3 per cent

7.1 per cent

10.5 per cent

The dew-point is

35°

40°

48°.

Collecting the dew-points calculated under the assumption previously made, in tabular form for convenience of inspection, we have:

With just enough air and the clay containing	Using		
	100 kg. of coal.	200 kg. of coal.	300 kg. of coal.
2.5 per cent combined water - - -	57°	50°	48°
5 per cent combined water - - -	65°	57°	53°
10 per cent combined water - - -	74°	63°	60°
With the double amount of air and clay containing			
2.5 per cent combined water - - -	44°	38°	35°
5 per cent combined water - - -	55°	44°	40°
10 per cent combined water - - -	63°	51°	48°

From this table we can deduce the law that the content of water vapor and therefore the dew-point of the fire-gases falls the lower (all other conditions being equal) the greater the consumption of fuel; that is, the harder the bricks are burnt and the greater the heat required by the materials to bring them to a condition of complete burning.

## II. QUANTITIES OF AIR AND HEAT WHICH ARE REQUIRED IN WATER-SMOKING

The fire-gases are, as has already been shown, the less suited to give up heat in the water-smoking process, the higher they are in water vapor; and the quantity of heat which must be obtained in some other way than from the fire-gases, for heating newly set brick to a temperature above the dew-point and later for dehydrating, them is the greater the higher the dew-point. On that account, the same factors which tend to increase the relative water content of the waste gases, will always have the effect of decreasing the possibility of proper water-smoking.

As such factors which are unfavorable to water-smoking, we have learned to recognize a high content of chemically combined water in the clay, and the combustion of coal with a small supply of air, that is, a factor which tends to increase the economic effect of the fuel to a maximum, unless the admission of air is not allowed to fall below a certain required minimum.

Now, since it is far easier to control the ratio between the fuel and the air of combustion, which gives the highest heating effect, in gas-firing than in the use of a solid fuel, especially when the latter offers only proportionately small areas of its surface to the attack of the air, and, since it is always endeavored to use the fuel as advantageously as possible, in gas-firing, for this reason, the danger of incurring bad effects through the waste gases will always be more eminent during the water-smoking process, than in the ordinary kilns. In other words, the care and precautions which must be exercised in order to guard against condensation from the waste gases before their escape into the main flue, all other things being equal, will be greater than is the case even in the ordinary continuous kilns.

If we assume, according to the average figures for continuous kilns, that the coal consumption amounts to 200 kg., and the average content of chemically combined water of brick clays is 5 per cent, and in the average double the theoretical air supply is admitted, then the average dew-point of the gases, that is, the temperature at which they are able to carry off as vapor all the steam generated by the burning of the coal and from the clay, without precipitating the water in the form of a fog or sweat, will be about  $44^{\circ}$  according to the preceding calculations, while the same temperature may rise or fall under favorable or unfavorable conditions to  $74^{\circ}$  and  $26^{\circ}$  respectively. The bricks must therefore be heated up to this point by some other source of heat, before the hot waste gases can be used for the heating and complete drying of the same, because contact with the cold brick will cool the waste gases to a point below this dew-point and thereby produce condensation in the newly set chambers. In order to avoid confusion, let it be understood that, with the appearance of condensation, bad effects do not

necessarily result, but under unfavorable conditions they will occur. Air-dry clay can take up more or less water in its pores, without seeming wet on the surface on that account, and affording opportunity for the lodgment of fine ashes or other impurities of the waste gases; on the other hand, if the waste gases contain acid vapors, these will likewise penetrate into the pores of the clay with the water, and will then exert an injurious influence on the color. But such a bad effect will not occur or only in a restricted degree, when water vapor begins to escape from the pores soon after the contact of the bricks with the hot waste gases. This will take place when the bricks are previously heated up to the dew-point of the fire-gases in such a manner that they are not harmed, that is, by special furnaces which allow the introduction of a quantity of air that is easily capable of carrying off all water vapors which are formed, as it is generally done in the water-smoking of the periodic kilns, and by the introduction of warmer air through the water-smoking flue in ordinary continuous kilns.

If we assume, therefore, that in the average the bricks in continuous kilns must be heated to  $44^{\circ}$  before they can be brought in contact with the fire-gases without suffering harm, and the bricks are brought to the kiln at a temperature of  $15^{\circ}$ , then a preceding rise in temperature of  $30^{\circ}$  in round numbers, must take place.

As a source of this heat, there are chiefly two factors which may be considered, namely, the heat supply which radiates from the still warm kiln walls and the kiln floor, and that which, if the first is not sufficient, can be brought in either through separate furnaces in the kiln door, or through special water-smoking furnaces above the firing shafts, or through the use of warm air, which can be taken from the cooling compartments by means of the water-smoking flues.

Before we proceed to the calculation of the quantities of heat and the air volumes needed to carry this heat and to carry off the water vapors produced simultaneously, it seems necessary for a better understanding, to explain first some of the conceptions and laws of the subject of heat, which are not familiar to practical men.

As is generally known, the thermometer is used for the determination of ordinary temperatures, and for higher temperatures the pyrometer, the construction of which we will assume at this time to be known, likewise the principles according to which the scales and their division into degrees are arranged. These apparatus have for their purpose only the indication of the intensity of heat, and give no measure of the quantity which is generated from a certain source, or is collected in a certain heated body. An example will make this plainer. Let us imagine any definite source of heat (for instance a gas flame or an alcohol lamp) which is used for heating a vessel filled with water, which is so constructed that all of the heat generated by the source can be conveyed to the water, losses being avoided. The vessel to be heated holds, say, 10 kg. of water, and the flame under it is capable of heating this 10 kg. of water in one hour from 0° to the boiling-point, that is, 100°. An experiment would now show that if the vessel held twice as much water at 0°, the temperature would rise only to 50°, and with 100 kg. of water the elevation of temperature would only amount to 10°. But in all of these cases, if it is assumed that the flame remains constant, the same quantity of heat has always been generated and has all been carried into the water, without giving, however, the same thermometer reading. The heat generated is therefore not expressed alone by the elevation in temperature which the thermometer shows, but also at the same time, by the amount of the water heated, and in such a manner that the number of thermometer degrees, multiplied by the kilograms of water, will give the same result in all cases.

In order to connect these two factors, temperature and quantity of the material heated, into one expression for the measurement of the quantity of heat given out from any source, it has been agreed to take as unity the quantity of heat which is capable of raising 1 kg. of water, 1° from 0° to 1°.

This quantity of heat is termed a heat unit or calorie. In the example shown above the quantity of heat generated by the gas or alcohol flame is expressed as 10 kg. × 100°, or 20 kg. × 50°, or 100 kg. × 10° = 1000 heat units in each case.

According to the statements made above, it will be apparent that, if we were to mix 1 kg. of water at  $0^{\circ}$  and 1 kg. at  $100^{\circ}$ , we should get 2 kg. at  $50^{\circ}$ . The conditions will be different, however, if we mix bodies of different kinds with one another, and the temperatures are allowed to equalize. If we mix 1 kg. of water at  $100^{\circ}$  with 1 kg. of mercury at  $0^{\circ}$  the mixture would not take on a temperature of  $50^{\circ}$ , but of  $98.8^{\circ}$ . This is due to the fact that all bodies do not require an equal quantity of heat to increase their temperature  $1^{\circ}$ , and that the quantity of heat which 1 kg. of mercury takes up is much less than that of 1 kg. of water.

Having taken water as unity, which of all known bodies takes up the greatest quantity of heat with the same weight in being raised  $1^{\circ}$  in temperature, the quantities of heat required to heat 1 kg. of a great number of substances have been determined by very subtle experiments. The numbers thus obtained are called the specific heats of the substances.

The following figures have been found to be the specific heats of the substances which are most important for our consideration:

Water	-	-	-	-	-	1.0000
Air	-	-	-	-	-	0.2669
Oxygen	-	-	-	-	-	0.2361
Nitrogen	-	-	-	-	-	0.2754
Carbon dioxide	-	-	-	-	-	0.2210
Carbon monoxide	-	-	-	-	-	0.2884
Steam	-	-	-	-	-	0.3010
Burnt clay <sup>1</sup>	-	-	-	-	-	0.2083

This means, that to heat 1 kg. of water  $1^{\circ}$  requires 1.000 heat unit, 1 kg. of clay requires 0.2083 heat unit, and 1 kg. of atmospheric air 0.2669 heat unit.

With this all the data are given, which are necessary to calculate the quantities of heat needed to heat a certain weight of a body a definite number of degrees, or to find the quantity of heat which a body loses, when it cools a certain number of degrees. It is only necessary, in order to express the

<sup>1</sup> An average of three sorts.

quantity of heat in heat units, to multiply the weight, expressed in kilograms, by the temperature difference, expressed in degrees centigrade, and by the specific heat.

A cubic meter of air weighs (at  $0^{\circ}$  and 760 mm. barometer reading) 1.299 kg. In order to heat 1 kg. of air to  $100^{\circ}$  C. there are needed:

$$1.299 \times 100 \times 0.2669 = 34.56 \text{ heat units,}$$

or as much heat as is needed to heat 34.56 kg. of water  $1^{\circ}$  or 1 kg. of water  $34.56^{\circ}$ .

In heating a brick weighing 3 kg. to  $100^{\circ}$  the necessary quantity of heat is calculated to be

$$3 \times 100 \times 0.2083 = 62.49 \text{ heat units.}$$

For an unburned brick which contains 3 kg. of clay (burned), 5 per cent or 0.15 kg. of chemically combined water and 5 per cent or 0.15 kg. of hygroscopic water, the quantity of heat which is necessary to heat it  $100^{\circ}$  is found to be

$$3 \times 100 \times 0.2083 = 62.49 \text{ heat units for the clay.}$$

$$0.3 \times 100 \times 1.0000 = 30.00 \text{ heat units for the water.}$$

$$\text{Total} - - - 92.49 \text{ H. U.}$$

It is known that, when water is heated in an open vessel, its temperature steadily rises up to  $100^{\circ}$ ; from this point on no rise in the thermometer takes place, no matter how much one increases the supply of heat, but all the additional heat is used for converting the water from the liquid to the gaseous state. Measurements have shown that while, as we have already seen, 100 heat units are needed to heat 1 kg. of water up to  $100^{\circ}$ , in vaporization a far greater quantity, namely, about  $5\frac{1}{2}$  times as much, or 540 heat units, is used which disappears as far as our senses and the thermometer are concerned. These 540 heat units are called the latent or hidden heat of water vapor. There are required, therefore, altogether, in order to change 1 kg. of water from  $0^{\circ}$  to steam at  $100^{\circ}$ ,  $540 + 100$ , or 640 heat units. Inversely, this latent heat is set free again as sensible heat on the condensation of the water vapor, for 1 kg. of water vapor in changing to liquid water gives up as much heat as is needed to heat 540 kg. of water  $1^{\circ}$  or 5.40 kg. of water from  $0^{\circ}$  to  $100^{\circ}$ .

It has further been proved that when water is changed into steam at temperatures below the boiling-point, the amount of latent heat remains the same, and only the sensible or free heat is diminished correspondingly. When, therefore, water at  $20^{\circ}$  evaporates, the heat necessary for vaporizing it amounts to  $20 + 540 = 560$  heat units, or at  $50^{\circ}$  to  $50 + 540 = 590$  heat units for every kilogram of water.

Let us turn back after this digression to the application of these laws to a given case. We had assumed that a brick clay contained on the average 5 per cent of chemically combined water, and that the green bricks had to be heated  $30^{\circ}$  before they could be brought in contact with the fire-gases of the kiln without bad effects. If we assume also that 5 per cent more water is contained in the air-dry bricks as hygroscopic water, then 1000 green bricks, which weigh 3 kg. burned, will consist of 3000 kg. of clay (burned), 150 kg. of chemically combined water, which is only driven out at a red heat, and 150 kg. of water which is expelled in the drying or water-smoking, or altogether 3300 kg.

The consumption of heat in heating up this quantity of clay from  $15^{\circ}$  to  $45^{\circ}$  is calculated as follows:

$$3000 \times 30 \times 0.2083 = 18747 \text{ heat units for the clay.}$$

$$150 \times 30 \times 1.0000 = 4500 \text{ heat units for the combined water.}$$

$$150 \times 30 \times 1.0000 = 4500 \text{ heat units for the hygroscopic water.}$$

$$150 \times 540 = 81000 \text{ latent heat.}$$

$$\text{Total} - - - \underline{108747} \text{ heat units.}$$

If this heat were generated by direct combustion, that is, by fires in the doors of the kiln, or by water-smoking furnaces, then the consumption of fuel necessary to produce this effect would be (since it was established that 1 kg. of coal of average composition generates 7487 heat units, 1 kg. of wood 3878 heat units on combustion)  $\frac{108747}{7487} = 14.5$  kg. of coal, or  $\frac{108747}{3878} = 28$  kg. of air-dry wood.

If this heat were conveyed through one of the water-smoking flues under the assumption that the temperature of the warm air entering the water-smoking compartment is  $100^{\circ}$  higher

than the same air after it had cooled down by contact with the bricks, the temperature of the air being  $145^{\circ}$  before and  $45^{\circ}$  after cooling, then, since we have seen before, that a cubic meter of air in order to be heated or cooled  $100^{\circ}$  will take up or release 34.56 heat units, there will be needed  $\frac{108,747}{34.56} = 3147$  cubic meters of air for every 1000 bricks.

The air used for this process will be drawn in through the open doors of the kiln chambers by the draft of the stack, carried through a part of the cooling compartments of the kiln, where it becomes heated, and is carried through the water-smoking flues to the drying compartment. If we assume that the outside temperature is  $15^{\circ}$ , the air from the water-smoking process would have to be heated from  $15^{\circ}$  to  $145^{\circ}$  or  $130^{\circ}$ , and this heat is to be drawn from the bricks undergoing cooling. A cubic meter of air weighs 1.299 kg. The quantity of heat which is carried out by 3147 cubic meters at a temperature increase of  $130^{\circ}$  amounts to  $3147 \times 1.299 \times 0.2669 \times 130 = 133,704$  heat units.

Since in the ring kiln, the operation must always be considered a regular one, this quantity of heat needed for the heating and drying of 1000 bricks must be taken from 1000 other bricks still remaining in the cooling compartments, in such a way that these give up their heat to the air used in the water-smoking. We have seen above that a burned brick, in order to be heated or cooled to  $100^{\circ}$ , gives or takes up 62.49 heat units. For 1000 bricks and  $1^{\circ}$ , this would amount to 624.9 heat units, and the number of degrees through which the 1000 bricks would have to be cooled by the air currents would amount to  $\frac{133,704}{624.9} = 214^{\circ}$ .

The preceding calculation (whose result is that in order to heat 1000 bricks  $30^{\circ}$  by means of hot air, and at the same time to evaporate the water contained in them, 1000 other bricks must be cooled down  $214^{\circ}$  by the heating of this air supply) establishes the maximum heat consumption and is true only under the supposition that the walls of the kiln compartments, in which the bricks are set, are thoroughly cooled down, so that the radiated heat need not be taken into consideration. In reality this

never takes place in regular work, but rather a very considerable quantity of heat for the preheating is furnished by this source, since experience has shown that the heat in many cases has sufficed alone to protect freshly set brick from any harm caused by the waste gases. The quantity of heat furnished by the walls is dependent on the area of the radiating wall surface and on its character, as well as its temperature and the temperature of the body which takes up the radiated heat, that is, the newly set bricks themselves.

The wall surface of a kiln chamber does not stand in a simple ratio to the kiln content, and it is proportionately larger the smaller the latter is. For example the wall surface, including the bottom or floor of a kiln chamber of 10 cubic meters' content, is calculated to be 21.5 square meters, for 30 cubic meters' capacity it is 44.5 square meters, and for 100 cubic meters it is 106.5 square meters. If one takes 280 bricks as occupying 1 cubic meter of kiln space he will find in the first case 7.7, in the second 5.3, and in the third only 3.8 square meters of radiating surface per 1000 bricks.

One will recognize from this that the heat of the kiln walls exercises a far greater and more beneficial influence in small kiln chambers than in large ones.

In order to study the influence of the warm walls more closely, let us assume such conditions as are found in practical work.

The temperature of the newly set bricks is, say,  $15^{\circ}$ ; these must be warmed before the admission of the kiln gases to  $45^{\circ}$ , without air circulation, between two dampers, and the temperature of the walls  $60^{\circ}$ . Let it be assumed that the hot, frequently glowing, masses of sand behind them, will replace to the thick kiln walls all the heat radiating from the surface, so that the temperature of the walls during the twenty-four-hour period remains constant to  $60^{\circ}$ .

According to the tables made in the investigation by Schinz,<sup>1</sup> it is found that, at the temperature conditions previously assumed, the square foot (equal to 0.09 square meter) radiates in

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<sup>1</sup> Schinz : Compendium der Waermemesskunst, Tables XLI and XLII.

one hour 43 heat units (reckoned to 1 pound and 1° C.) which makes per twenty-four hours and per square meter (reckoned as heretofore to 1 kg. and 1°), 5375 heat units. In a kiln of 10 cubic meters, capacity per chamber, the radiated heat for 1000 bricks would amount to  $7.7 \times 5375 = 44137$  heat units; for a chamber capacity of 30 cubic meters, there would be  $5.3 \times 5375$  or 30,375 heat units; and for a chamber content of 100 cubic meters only  $3.8 \times 5375 = 22,804$  heat units.

If no change of air occurs in the preheating, as has been assumed to be the case, then no evaporation of the water contained in the brick will be possible during the heating, and therefore no consumption of heat will take place in the form of latent heat or evaporation. If we deduct the latent heat from the quantity of heat previously calculated for the heating of 1000 bricks to 45°, there will remain still 27,747 heat units which are necessary to effect the heating of the bricks through 30°.

We can see from this, that with a kiln capacity of 10 cubic meters, the radiated heat from the walls is considerably greater in amount than necessary, and with a kiln capacity of 30 meters it is still sufficient to effect the assumed heating of the kiln contents from 15° to 45° and is too small only in the case of the largest kiln.

If the heating and water-smoking is simultaneous with a change of air, so that the air is the carrier of the ingoing heat and at the same time the carrier of the water vapor generated, then the heat consumption is much greater on account of the additional latent heat due to the evaporation of the water than when the heating is accomplished only by the radiation of the kiln walls; but the quantity of heat thus obtained must in this case be deducted from the total requirement. In this manner we have, when the water-smoking is effected by direct fire or air, for a kiln of

Chamber capacity 10 cubic meters, 64010 heat units	per
Chamber capacity 30 cubic meters, 78362 heat units	1000
Chamber capacity 100 cubic meters, 85933 heat units	bricks.

If we calculate in the manner above given the quantity of air which is necessary for the transportation of this heat, under the

assumption that the air entered 100° hotter than it went out, we will obtain 1852, 2264, and 2486 cubic meters, respectively. If we compare these figures with those which are obtained in the calculation of the air requirement for burning the fuel, we will see that in many cases the air consumption in the water-smoking process is greater than for the burning process itself, under the assumption that only absolutely air-dry bricks are set, and that accordingly one must take into consideration, not only in the construction but also in the operation of the kiln, that the air circulation in the water-smoking compartments is to be the liveliest possible. It is thus explained, how in many cases the water-smoking and the air flues which were first built in small dimensions proved to be insufficient, and made necessary the simultaneous use of other appliances, like portable water-smoking furnaces. The later, bottom water-smoking flues in the Hoffmann kiln, which can be built far larger than those higher up, are now able to accomplish the transportation of the air and heat.

If we assume that, in a filled kiln, 280 green bricks are set in a cubic meter, and that 0.6 of the space is taken by these and 0.4 by the air spaces, flues, and firing shafts between them, then the space which 1000 bricks take up in the kiln is calculated to be  $\frac{1000}{280} = 3.57$  cubic meters, and the air space, which remains between the bricks, amounts to 1.43 cubic meters. Since we have seen above that under the assumed quantity of moisture which must be taken out of the bricks in a twenty-four hour water-smoking period, respectively 1852, 2264, 2486 cubic meters of air which can give up 100° of heat, must be brought in contact with 1000 bricks, the ventilation must be sufficient to renew the air in the  $24 \times 60$  minutes  $\frac{1852}{24 \times 60} = 1.28$  times in the first case,  $\frac{2486}{24 \times 60} = 1.72$  times in the second case, per minute.

For such a vigorous change of air (which is always to be regarded as the minimum, since the assumption that only air-dry bricks go into the kiln is only occasionally carried out in practice), sufficient facilities exist in the older kilns, allowing

the air to enter the kiln or escape from it laden with moisture. It is the rule that in water-smoking, not only the fire-holes, but also the numerous holes in the arch, are wide open. But in the continuous kiln similar conditions must also be attempted, and practice has already shown that a small fire in the door of the chamber, especially in large kiln chambers, as well as water-smoking flues consisting of a few narrow conduits for hot air, have often only been partially successful ; and in the use of materials which are very apt, owing to their physical and chemical properties, to become discolored, they generally do not exert any influence worth mentioning.

But it is evident from what has been said, that when air, having a temperature difference of  $100^{\circ}$  between its temperature when admitted for drying and when it escapes cooled and saturated with moisture, is to be used, a very complete use of all means must be made, which will serve to produce a movement of air in the kiln chamber : such means are generally the chimney and dampers ; and it should be laid down as a rule that the damper which connects the chamber, being preheated with the main draft flue, should be wide open during the entire water-smoking period. If we take warm air from the cooling compartments, in which the temperature is not very high, we need not fear an ill result to the bricks from a too rapid heating with the small amount of heat which dry air is able to carry. Besides, one is always able to take the warm air in the beginning from a point in the kiln where the temperature has been lowered below  $100^{\circ}$ , so that in every case a slow heating is assured.

If we consider the different methods of preheating and drying off bricks in continuous kilns, before they can be brought in contact with the waste gases of combustion without ill effects, only from the economic standpoint, then without doubt that method stands first in which the bricks are enclosed between two dampers, and are heated by the radiating heat of the kiln walls, without allowing a change of air, to a certain temperature, which must lie above the dew-point of the fire gases; and we have seen that this heat under favorable conditions, that is, in kilns of small dimensions and regularly operated, is amply sufficient to

attain the end in view. Still it is always necessary to retain, as far as possible, the heat which the kiln walls must always take up, and not to lose a great quantity of heat by a too hasty removal of the doors or by opening the firing-holes in the empty or part of the cooling compartments. But at this point there is the fact to be taken into account, that when the heat of the kiln is retained as much as possible, especially in low arched kilns, the temperature of the compartments in which the workmen are compelled to stay is often very high.

For this reason in many places operations are not carried to the extreme utilization of heat, and water-smoking either is not carried on at all and the production of good colors neglected (the easiest but also the most un rational way), or an extra amount of fuel is used for separate water-smoking, making it more pleasant for the workman and giving better sanitary conditions. The use of water-smoking flues, by means of which all heat which otherwise escapes from the kiln through the firing-holes, offers a successful mode of water-smoking, without expense for fuel; however it requires more work and more intelligence, as well as greater care, if it is carried out on a large scale. The use of the water-smoking flue offers the advantage, not to be underestimated, that the ventilation in the chambers in which work is carried on is much stronger than when only the air necessary for combustion is drawn through the kiln, thus making the conditions for working more agreeable without causing any loss of heat owing to the opening of the firing lids. It will be necessary to make use of special furnaces in the doors, or better above the firing-holes, only where in building the kiln no attention was given to the construction of a water-smoking flue, or where the latter was built too small for conveying the very large volumes of air necessary, as we have seen, or again, where the subsequent introduction of such an aid (the most advantageous location being beneath the kiln floor) is not practical. These separate furnaces will, of course, give rise to an extra expenditure of fuel, but when a large volume of air is used they will produce the same favorable results as a water-smoking flue that has correct dimensions and is properly operated.

## Continuous Kilns Fired With Gas for Burning Clay Wares

W. H. ZIMMER, PH.D., TRANSLATOR

Mr. Mendheim, engineer of the new gas kiln constructed for the Royal Porcelain Factory at Charlottenburg, is the author of a paper which appeared in No. 16 of the *Deutsche Bauzeitung*, 1872, and in which he draws some comparisons between this kiln and the continuous kiln. I cannot entirely agree with him in these comparisons which for this reason I desire to subject to a further discussion in order to clear up the matter for the benefit of the clay industry.

It remains an undisputed fact that the Hoffmann kiln has led to a momentous revolution in the clay industry, and especially in the manufacture of brick in a very few years. For this reason it is to be classed among the most important inventions of modern times, economically considered, and it has given its inventor an honored name far beyond the boundaries of the fatherland. Not only its extensive distribution (800 kilns at the present writing) in all branches of the clay industry, but also the fact that all those kiln constructions for pottery purposes which appear of late, and have as their aim economy of fuel, follow more or less closely the fundamental idea of the Hoffmann kiln. However, in the manner of firing and the shape of the kiln spaces, great variations are often found, conditioned by the nature of the ware to be burned or by special results which are desired to be obtained. The foundational principle underlying the Hoffmann kiln is the continuous fire progressing in a closed ring, with maximum cooling of the fire-gases and use of the heat stored in the burned objects for preheating the air used for combustion. The new continuous gas kiln evidently belongs to this category of burning apparatus.

The continuous kiln suffers the fate of all great inventions, having at the beginning been declared impractical and visionary by laymen and technical authorities. When finally the inventor, after tireless study and great sacrifices, furnished the proof that

it was bound to give the best results in spite of the technical objections raised when operated properly, there were soon found, on the one hand, enthusiastic admirers and on the other ignorant and envious people. The latter class attacked him in the lowest manner and endeavored, with the assistance of the peculiar conception of the dispute on the part of the Prussian patent commission, to take away from him not only the credit for the invention, but even tried to show him to the world as one of the most desppicable examples of a plagiarist.

I do not include Mr. Mendheim in this category of enemies of the continuous kiln; Mr. Mendheim has earned an undisputed recognition for himself in the clay industry through his studies in the erection of the new plants of the Royal Porcelain works, and hence his views, since they are of weight to the manufacturers interested, cannot be overlooked.

In the introduction to his paper, Mr. Mendheim refers to the great advantages which the Hoffmann kiln offers for the production of common brick, but claims it to be of no value for the burning of better products, finer clay wares, face brick, and even for the better kinds of common brick and clinkers. He advises that for such products it be replaced by the continuous kiln fired with gas according to the system of the Charlottenburg porcelain kiln. Facts speak the loudest and in order to prove Mr. Mendheim wrong it would only be necessary for me to mention to him a long list of plants in which good building and face brick are produced in the continuous kiln; I might go still farther and bring to his attention the fact that the famous Oldenburg clinkers also are produced in about half a dozen kilns, that the stoneware factories in Ziesar, Belgern, Goerzke, Ober-glauche and Krummnussbaum use the same system for glazed products, that English factories burn in it salt-glazed fire clay products and that one of the most important stoneware and faience factories in Lorraine is at present building a continuous kiln for burning in it its products, enclosed in saggars, after tests made in another kiln had furnished favorable results. This will help to prove that it is not always necessary to lose the great saving in fuel in consideration of the quality of the products.

It cannot be denied that, of course all these factories had to struggle with great difficulties at the beginning, as is the case with all new improvements, difficulties which the gas-fired continuous kiln would also meet in its introduction in the porcelain and brick industries, and from which, even to-day, a large number of brickyards suffer, that are not able to produce even a common brick of ordinary quality. But if the manufacturer of a higher grade of products has succeeded in overcoming the difficulties and in the correct knowledge of the peculiarities of the kiln has been enabled to find a way which unites fuel economy with the burning of good products, it may be expected that others with their lower grade products might arrive at the same result after once the necessary intelligence which so far has been missed very much, has taken its place among the clay workers. But at any rate it does not appear justified to give expression to such a sharp judgment as Mr. Mendheim does, now when our industry is only beginning to rise.

The fault with which the continuous kiln is reproached by many, and which has been especially brought out by Mr. Mendheim, is that it is said to be impossible to burn such products in this kiln which must be of a uniform color, and that hence it is often necessary to lose the advantages of the system of continuous burning with direct firing, in order not to lower the quality of the products. This may be true for glazed ware, with the use of a fuel high in ash, but this trouble does not occur in the measure which Mr. Mendheim imagines, for a sensible manufacturer will not use peat, but a pure grade of coal or wood for the open burning of glazed wares, no matter what may be the construction of the kilns. That reproach holds true only when, as is often done, the unreasonable demand is made of the continuous kiln to produce the best products with the possibly worst fuel obtainable; I believe Mr. Mendheim would be perplexed by such demands, even with the gas kiln, though not as much as with the ordinary continuous kiln.

All the discolorations of the surfaces of brick burned in the continuous kiln are ascribed unjustly to the ashes, and though this is true for the ware which comes in direct contact with the

fuel, still this is not the cause of all the discolorations, but their cause is for the greatest part to be looked for elsewhere. It is not difficult to prove that most discolorations on unglazed products are connected with the nature of the fire-gases, and the degree in which the heat produced is utilized. This must also be true of the gas-fired continuous kiln, unless the same precautions are taken which are necessary in the ordinary continuous kiln and whose neglect makes itself felt in the manner which Mr. Mendheim considers inherent in the system. In gasifying the fuel, the ash is removed from the burning space proper, but not all the other, much more important, influences; the chemical action of the flame is not changed, nor are there removed the gaseous impurities of the fire-gases evolved in all furnaces, since for obvious practical considerations the gases cannot be purified.

Whoever wants to take the trouble of examining the surfaces of a brick by means of the magnifying glass or microscope will be able, without difficulty, to recognize what discolorations have been produced by ashes and those which must be ascribed to other causes. It will be seen that all ashes which are not found on a clinker burned to complete vitrification, can be easily recognized by their cellular structure or when originating from coal, by their slaty, or splinter-like, or partially fused appearance, and can be removed more or less easily by rubbing or washing. The observer will further perceive that non-removable coatings appear especially on such products which possess a dense and smooth surface, unfavorable to the deposition of ash. This is especially true of machine-made brick and common brick molded in water and face brick, but never or seldom of brick molded in sand, with a rough surface. I would ask Mr. Mendheim to observe that machine-made bricks often have thick coatings on their smooth surfaces, while the depositions either are slighter on the surfaces roughened by the wire, or are entirely lacking. Although these phenomena force us to a more extensive study, still they show with certainty even at this stage that in the majority of cases the ashes are innocent of causing the discolorations in question. Even the products of the Flemish

and Lower Rhenish brick industry so miserable in shape and durability, which are produced in clamps in direct contact with the fuel, do not show those striped discolorations, not even on accidentally produced clinkers, which we often find on products burned in more perfect kilns. This furnishes the proof that the ash plays an insignificant rôle in the discoloration of the surfaces of unglazed products. On the other hand it may be observed in kilns of any construction in which there are found discolored or clean colored face brick that the surfaces of the brick are dusted with the finest ash without being damaged in regard to color.

Since it may appear a venturesome attempt to contrast an apparatus, concerning which the possibility of obtaining good results has been shown by a great number of examples, with one which, as far as known to me, has been constructed and is operated in but one instance, it will be necessary to produce more proofs for the latter, especially because it has been applied only for the production of the highest temperature at all obtainable in technical works. But at the same time well founded objections are admissible as to whether the comparatively low temperatures of the other branches of the clay industry can be distributed throughout the entire kiln space with the same certainty and uniformity; the question is, whether or not the same difficulties of irregular heating, which are inherent in the older kiln constructions, will show themselves here in a still more pronounced degree. Neglecting this objection, which can be proved in the wrong or be confirmed only by practice, it is not difficult to furnish the proof that all the phenomena of discoloration must necessarily appear in the same manner with the use of gas as they are attributed to the Hoffmann continuous kiln, in so far as the principle of the extreme utilization of heat is maintained and the precautions are neglected which also must be observed in the ordinary continuous kiln. At any rate it must be admitted that the more complicated gas kiln is more difficult to operate and to regulate than the ordinary continuous kiln, and the latter, indeed, offers difficulties enough and puts the intelligence of the workmen to a severer test than the periodic kilns.

If Mr. Mendheim would inquire of manufacturers of buff

brick whether any kind of fuel could be used in their manufacture, he would be informed that the selection of fuel is of the greatest influence upon the color in all kiln systems, and that it happens—wood being, in general, excluded as a fuel—that in this case the fuels highest in ash (peat and lignite) are especially favorable, while coal only rarely permits the production of uniformly colored brick. Coal gives rise to red discolorations on the exposed surfaces which penetrate frequently several millimeters into the clay mass.

Not only the red color alone, but also the thickness of the colored layer, excludes *a priori* the influence of the ash, and there remains as the only explanation of the phenomenon a chemical reaction of several constituents of the fire-gases upon the clay. Chemistry teaches us that all clays high in iron which in a certain stage of vitrification assume in burning a yellow or white color must always contain an amount of calcium carbonate which stands in a definite relation to the iron, and that by the formation of a light-colored iron-lime silicate the otherwise red color of the brick due to the iron oxide is hidden. If now the lime on the surface enters into another combination so that it cannot unite to form the light colored compound mentioned above, the coloring power of the iron will appear in its full strength. This case can very frequently occur in practice and will then always be characterized by a red coloration, if a stronger acid than the silicic acid is brought in contact with the lime during the burning, and this is accomplished in the easiest way, if at the beginning of the firing water vapors can condense upon the surfaces of the brick. In using coal the fire-gases formed are never lacking in sulphurous acid which, with the cooperation of hydrogen and oxygen, likewise always available near the objects to be burned, converts the calcium carbonate on the surface to the sulphate and thus robs the lime of the possibility to enter into the light-colored lime-iron silicate combination, or removes this possibility to a temperature beyond the practical limit.

The gas is not to be considered as an independent fuel with definite chemical properties, but its composition is in the first place dependent upon the nature of the solid fuel from which it

is produced, and there will always be found a chemical difference between coal, lignite, and peat gas, since with the exception of the solid residue all the volatile constituents of the solid fuel are contained in the gas. To these volatile substances there belong beside the carbon, hydrogen, oxygen, and nitrogen, also sulphur, and hence the latter, in all processes where it may exert an injurious effect, will do so whether the fuel is gasified or not.

A very essential difference between the kilns operated continuously (which include the gas-fired continuous kiln) and the older kiln systems, consists in the fact that the heat developed in the former is utilized to the maximum, and in the last stage serves to dry the wares freshly set in the kiln, while in the latter the fire-gases reach the outside after a short passage at a very high temperature, and the drying or water-smoking is considered as an independent operation at the beginning of the burning. But this economical use of the waste heat—and this cannot be avoided by a change in the shape of the kiln or the use of a different fuel, not even of gas—is accompanied with difficulties during water-smoking which require special precautions whose neglect will cause the same consequences in the gas kiln which are experienced in the Hoffmann continuous kiln and all its allied kiln systems, but which can also be avoided.

In the kilns of older construction the objects to be burned come in contact in the first stage of burning, that is, in water-smoking, with a large volume of moderately heated dry air which removes the hygroscopic moisture with great ease; in the continuous kiln, however, the quantity of air is restricted to the amount which just suffices to maintain the maximum firing; it also is not dry, but contains as vapor all of the large quantity of water chemically united with the clay substance which is expelled in burning. Now the cooling of the moist fire-gases can be carried only to a certain limit without injuring the kiln contents; if, on continued cooling by contact with the freshly set bricks and the absorption of heat conditioned by the constant evaporation, the point of saturation of the air with water vapors is reached or exceeded, then finally a periodic condensation must

take place, and this may occur, under conditions particularly favorable in this respect, to such an extent that the kiln contents are partially softened.

If the greatest possible fuel economy is the only aim in the operation of the kiln, then such a periodic condensation will be the rule in the gas kiln like in all other continuous kilns, that is, the freshly set cold bricks will "sweat" in the moist atmosphere of the water-smoking chamber, saturated with water vapor, and every brickmaker knows the consequences of this. There is produced on the surface a whitish, firmly adhering coating, and from what has been said above it appears sufficiently clear why this takes place less frequently in the older kilns than in the continuous kiln. On examining the nature of these coatings more closely we will not only be able to recognize the reasons why these are more easily produced on the dense surface of the face-brick than on the rough surface of the common brick, molded in sand, as I have mentioned above, but we will also be able to find means of preventing them unless they have already been produced during the drying, which is often the case. In the latter case, of course, the cause of the discolorations can not be removed by burning.

On examining the efflorescence in question with a magnifying glass it will appear as wart-like or scaly or blistery masses, quite similar in appearance to those which are found on air-dried as well as on very soft and very hard brick and whose characteristics disappear gradually only when the clay has assumed the vitreous condition, that is, when it is partially fused. Of what nature this efflorescence is, has not yet been determined by chemistry. This is very likely due to the fact that a sufficient quantity of the pure material can be obtained only with difficulty; but microscopic examination has shown that it is not a deposit of ash, which, when also present, can be recognized with certainty, but that it is composed of residues, partially crystalline, which, at one time in solution, have been deposited in the solid state on the evaporation of the water upon the surface of the brick. The efflorescence may also have been caused by the residue left by water taken from the clay in water-smoking and condensed on the sur-

face. Salts which could produce such an effect and which are so changed in burning that the residue is not dissolved by water, are plentiful. Calcium carbonate and calcium sulphate are present in most clays in such quantities that the water in the brick may be considered as a saturated solution of these salts; chlorine compounds, especially salt, are hardly ever lacking. Iron sulphide, a very frequent constituent of clay, decomposes during the drying and together with the other insoluble constituents forms ferrous, aluminum, and magnesium sulphates. In addition to this, on taking up water during the first stage of water-smoking, ammonium salts, alkali salts, and sulphurous and sulphuric acid, are condensed from the fire-gases, and if precautions are not taken to prevent such a condensation a considerable concentration of soluble substances takes place on the surface of the brick.

On the evaporation of the water all the dissolved substances must, of course, remain in the solid state and where this takes place will depend solely upon the character of the evaporating surfaces and the manner in which the water is removed. With a dense clay mass and slow drying the evaporation of water can take place at the beginning only at the surface ; but the fluid contained in the pores will always be able to diffuse towards the interior and equalize its higher content of salts from the outside with the lower of the interior liquid, till with further drying the pores open and evaporation with final deposition of salts will also take place within the clay mass. With lean material or with a porous surface this evaporation in the clay will take place sooner and hence brick with rough surfaces are less liable to show efflorescence. If evaporation takes place rapidly or, still worse, if owing to condensation on the surface the pores are again filled with liquid, diffusion cannot take place in the short time owing to the strong flow of liquid and vapors from the interior and all the substances dissolved in the water must be deposited on the surface and the more so the denser the latter is.

It is thus seen that the discolorations caused in this manner, and these form the majority of phenomena of this kind, appear in drying and water-smoking, but have nothing to do with the

burning process proper. Unless the same favorable conditions are created which exist in the older kiln constructions, the use of gas, even if purified, would not be a preventative.

These ways have been partially followed in the case of the continuous kiln and they have led to the best results, removing the difficulties which gave rise to complaints. If Mr. Mendheim had had opportunity to study the English brick architecture and the manufacture of front-brick in Middle England, Yorkshire, Chestershire, and Leicestershire, with their continuous kiln plants, without any dryers whatever, where the brick are pressed from semi-dry clay powder and are trucked directly from the machine to the continuous kiln, still producing pure colors, I hardly believe that he would have been tempted to make such assertions as he did in his treatise.

It is not my intention to make a comparison between the Hoffmann and the gas-fired continuous kiln considered from all sides; the experience which has been had with gas-firing is not yet sufficient to draw conclusions; but I cannot fail to state that important theoretical considerations oppose the use of gas for comparatively low temperatures and practical experience alone must show how these are to be overcome.

It is nevertheless true that the gas-fired continuous kiln certainly has a great future in the porcelain industry and the branches of the ceramic industry adapted for its uses, and we owe thanks to the Royal Porcelain Factory and especially to Mr. Mendheim for having made a breach in this direction for the benefit of private industry. The difference between the burning of porcelain and its all leveling fusion and the manufacture of products with a porous body is so great that the experience obtained in the former direction can be applied only with the greatest caution to other branches of the clay industry. But until better results have been obtained in this direction, the Hoffmann continuous kiln will retain its place, which it has won, in the brick industry.

### The Failure of Gas-Firing at Greppin

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I have already treated the Greppin material in a previous paper which appeared in the *Notizblatt*, and have on that occasion pointed to the fact that continuous burning in itself offers greater difficulties in the way of obtaining good colors than periodic burning, and requires special treatment which was not necessary with the old kilns, in order that the influence of the fire-gases may be so directed that the surfaces are not injured in color by chemical or mechanical action. On this occasion I have chosen as an example the Greppin clay, because it belongs to those which show the influence of the fire-gases in a greater measure than the average clays. I will admit cheerfully that if in place of the Mendheim gas kiln a Hoffmann continuous kiln had been chosen, very likely, difficulties would also have been met at the beginning which, however, would not have been primarily due to the system, but to local conditions, to the peculiarities of the clay and lignite, and which could have been removed if the causes of the failure could once have been made clear.

The discussions at our conventions during the last years have given us many opportunities for speaking about gas-firing, and Mr. Mendheim, as well as other gentlemen who have used his system, have made communications in regard to its faults and successes. I believe that in using gas for ceramic purposes many have been led to erroneous views, because it was wrongly maintained that for obtaining a pure flame it is only necessary to gasify any, otherwise unsuitable fuel, thus eliminating the injurious effects upon the color of the clay. This illusion has been removed by practice in several cases in a somewhat harsh manner. The attempts which have been made to use generator gas produced from the best fuels (to which, in most cases, it was necessary to fall back, for the burning of common brick, face brick and terra cotta, lime and cements), appear to me to be wrong, because there is no absolute necessity to accomplish with

a complicated apparatus, always connected with heat losses, what can be done better and cheaper by the direct way. When good coal is at hand more is accomplished, economically, by direct firing in continuous, as well as in periodic, burning than with gas-firing. The wares of the Siegersdorf factory furnish proof that with careful operation the higher class products of the clay industry can also be produced in the ordinary continuous kiln, at the same time taking advantage of the economic results which the continuous kiln offers before all other burning apparatus.

The main point of gas firing in all industries lies in the utilization of low-grade fuel which, on account of its high content of ash, its content of water and impurities, as well as owing to its form, does not produce the required heat effect. For this reason I shall regard gas-firing as justified for ceramic purposes only where local conditions point to the use of a low-grade fuel and where products of greater commercial value, especially such from which ashes must be absolutely excluded either owing to the higher temperature required, or to glazed surfaces, are manufactured. Formerly, difficulties were met in producing the uniform current of gas required, but I believe that now by the use of blowers these have been removed.

From the very start a correct conception of the effects which the separate constituents of the gas exert was not had and it was believed that if only the ash is removed all discoloring influences are done away with also. But has really the quality of the fuel been changed by gasification? Is there not present the same quantity of steam, volatile sulphur compounds, ammonium salts, alkali vapors and perhaps of other impurities which are present when the low-grade fuel is burnt on a grate? And are not the constituents mentioned those which exert the most injurious effects owing to violent chemical reaction, and hence are to be feared more than the ash? These constituents cause the difference between the flames of fossil fuels and wood. The chemical reactions of the flame and especially the volatile impurities exert exactly the same influence whether the low-grade and impure fuel is burnt in the shape of generator gas or

by direct combustion; in fact, the effect is stronger with the gas, as has been shown by practice and of which I have convinced myself by corresponding experiments. I believe that satisfactory results will be obtained with gas-firing only when it is possible to produce gas from low-grade fuel, removing from the former the injurious constituents before introduction into the kiln. It is my opinion that the failures at Greppin and other places are to be referred to this cause.

The fuel which is to be considered mostly in regard to gas-firing under the conditions of Northern Germany is first of all the earthy lignite, and I would like to show the composition of a gas made from lignite by a numerical example. The moisture of earthy lignite at the mine amounts to 60 per cent of its weight. If the coal is exposed to the air the moisture content is decreased but never falls below 25 per cent; at the same time it is very dusty; and the kind designated as dry coal, contains on the average 40 per cent of hygroscopic water. Supposing that this lignite with 40 per cent of water is gasified under theoretical conditions, that is, burnt to carbon monoxide by a slight admission of air, the combined hydrogen being changed to volatile compounds, and the free water evaporated, there is produced a gas which beside nitrogen contains 26 per cent. by volume of steam and only as many, 25 per cent, of combustible gases. As Mr. Mendheim has given the consumption of coal at 16.5 hectoliters per thousand it can be estimated how much steam from the fuel is added to that which results from the chemical and hygroscopic water of the clay during the burning, and practical experience has taught in all branches of the clay industry what injurious influence is directly and indirectly exerted upon the products by water vapor.

When we consider the coal consumption of 16.5 hectoliters as given by Mr. Mendheim we arrive at a consumption of about 8 cwt. of coal per thousand, assuming the hectoliter of lignite to be equivalent to 150 pounds and its heating value to be one-third of the average heating value of coal. This quantity represents little or no saving as compared with the old kiln. The prospect of obtaining better colors does not exist for the gas

kiln, and this is especially true when using fuel which has not been dried. Hence there remains for gas-firing beside the utilization of low-grade fuel also the task of saving fuel and this is not accomplished by gas kilns built after the type used at the Royal Porcelain Factory.

I am not an enemy to gas-firing on principle, but I am opposed to the Mendheim kilns as far as the brick industry is concerned because I believe that they do not offer the conditions which permit very great economic advantages compared with the older kiln systems. Gasification in itself is associated with a loss of heat and other branches of industry have shown us that gas-firing can show economic results only when it is connected with regeneration, that is, heating of gas and air before their union, by the waste heat of the furnace. But this is true of the Mendheim kiln only to a very limited extent, for only the air but not the gas is preheated. Furthermore, the construction of the kiln is such that the quantity of heat stored in the burned ware and the walls is much greater than that which can be utilized for heating the air taken to the fire and must be allowed to escape unused. The continuous kiln offers in this respect much more favorable conditions for fuel economy since with the same capacity at most only half of the masonry is to be heated and it would be possible to preheat not only the air but also the gas. It is my opinion that it would be a thankful task for technologists to solve the problem how to change the method of firing as practiced in ordinary continuous kilns to firing with gaseous fuel. I am well aware that attempts in this direction have been made for a long time but I believe that these are not of moment since they are based upon wrong assumptions in regard to the movement and distribution of gases in the continuous kiln. Of late I have worked upon this question a good deal, in connection with the examination of the fire-gases in the continuous kiln, and I believe that it is certainly possible to arrange the latter so that the uniform distribution of the gas, throughout the entire kiln space, throughout the entire vertical section and consecutive positions, may be accomplished and also the preheating of the air and gas brought about before their union takes place. In this

way the economic advantages of the ordinary continuous kiln would, without doubt, be more nearly realized than has been possible with the gas kilns constructed up to the present time.

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### The Firing of the Continuous Kiln

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Keeping in mind the direction of the current of air in the continuous kiln and the charging of the fuel in a manner corresponding to the direction of the draft, it is seen that it is difficult to distribute the fuel so that its planes are perpendicular to that of the flow of air. Here the air is subject to the effect of two forces, to the effect of the upward motion due to the lower specific gravity of the heated air, and to the horizontal flow caused by the action of the stack. In the different parts of the kiln the conditions governing the movement of the air are very different also, and for this reason one or the other of the acting forces will preponderate and direct the general direction of the air current. The air always enters the empty part of the kiln, flows through the kiln tunnel and strikes the objects which give off their heat, increasing the temperature of the air. Since in general the kiln tunnel possesses a higher temperature than the outside air the latter on entering the kiln will at first keep to the kiln floor, flowing along it and rising in the degree in which it is heated by the contents of the kiln. When this rising movement has attained equilibrium with the horizontal one there will gradually take place an essentially horizontal flow of air in the parts of the kiln which are at maximum heat. Farther on in the portions where no more fuel is brought in contact with the air, cooling takes place. The resistance, which in the friction through the kiln contents is opposed to the movement of air, becomes continually less the nearer the air comes to the stack-flue. The closer the air approaches the exit the more will it be

under the influence of the stack, and it will flow directly towards it.

In the back portions of the kiln a second process takes place; here bodies must be heated which consume a large quantity of heat without being heated in proportion to this heat absorption, since this is utilized in removing great quantities of water from the ware, whose vapors must be taken from the kiln by the shortest route. Supposing the back part of the kiln to be filled with green bricks whose temperature is to be raised to  $100^{\circ}$ , we must expel a quantity of water whose expulsion in the form of steam consumes, without raising the temperature, five times as much heat as is required to heat this water to  $100^{\circ}$ .

This presence of moisture will cause a rapid cooling of the air and the latter will become more or less saturated with water vapor; the cooled air, laden with aqueous vapor is, however, heavier than warm and dry air, and hence will keep to the lower parts of the kiln, while that portion of the air which on its way had no opportunity to come in contact with objects giving off steam, will fill the upper parts of the kiln space. For this reason we observe in the last chambers quite a different distribution of heat than in those closer to the fire. The gases, under the effect of the draft and the decrease of frictional resistance, descend in the lower part of the portion of the kiln which is being fired; hence we observe that here the heat progresses most rapidly along the floor, but in the water-smoking chambers we find the highest temperatures on top. It is thus a phenomenon which at first might appear puzzling, and for which an explanation is not found at once, but which becomes perfectly clear when one considers the difference of the effect brought about by the flow of heat in the already highly heated portions of the kiln, and in those in which it comes in contact with bodies giving off water vapors.

If fuel is thrown into the continuous kiln through a firing-hole and the ware is set in such a way that the coal does not fall directly to the floor but is distributed uniformly along the walls of the firing shaft, thus making a vertical firing-flue, it will

be possible to produce a uniform mixture of air and combustible matter in all parts of the kiln. But if, from the start, care is not taken that such a distribution can take place the fuel, following the laws of gravity, will accumulate in the lower portions of the kiln and the combustible gases evolved, which in general take the same direction as the air, will not be able to mix with the latter in the desired degree. In this manner often a more intense heat is developed at the kiln floor than was intended; on the other hand, air may pass through the upper portions of the kiln without coming in contact with the combustible gases. The air simply meets no fuel on its way or only an insufficient quantity, and the case which I have previously discussed (that a loss of heat takes place in the upper parts owing to excess of air, and in the lower parts owing to a deficiency of it) may easily occur.

The production of a uniform temperature in all parts can be attained under no circumstances with a horizontal draft; only when care is taken that the fuel is distributed throughout the entire cross section in proportion to the regularity of the air circulation will it be possible to attain uniform conditions for combustion and with them the highest heating effect. For this reason the many kiln constructions of the present time must result in failures if they neglect these first conditions.

How is it possible to obtain such a uniform distribution of coal in the vertical direction when it is the natural tendency of the coal to fall to the floor? The principle of distributing the coal along the vertical walls of the firing-flues seems quite clear, but the practical difficulty is the overcoming of the law of gravity. And yet the fuel must be distributed as uniformly throughout the kiln as the air which passes through it. I have often taken pains to examine plants which give good results with the continuous kiln, and theory was confirmed inasmuch as in such plants a more or less suitable arrangement for the distribution of fuel was found.

But in most cases, namely, everywhere where complaint was made in regard to irregularity of burning, this complaint could be traced back to a lack of uniformity in the distribution

of coal; and occasionally the most nonsensical experiments—of course, without success—were undertaken, while a little knowledge of the subject in hand and moderate thinking, would have readily led to the right way.

In most cases the kiln is so operated that the air passes through the upper portions of the kiln without coming in sufficient contact with the fuel or combustible gases, and in consequence the lower parts are as a rule burned harder. For this reason, a continuous kiln, as I have indicated it in principle, can never be fired from the bottom, but always only from the top, since the fuel must be uniformly distributed at the top as well as at the bottom, and this can naturally only be accomplished by firing from the top.

I have often taken the trouble to instruct those who work with continuous kilns, but in nine times out of ten they continued to work as they should not have done, and to this fault must be ascribed the many failures which have been met in the operation of the kilns. This is especially true where the continuous kilns came into the hands of workmen who were accustomed to work with horizontal drafts and did not possess sufficient knowledge to transfer the experience obtained with the old kilns to the entirely changed conditions of the ring kiln. This does not indicate exactly a high degree of intelligence among clay workers.

I shall show the way of firing properly to those who are desirous of obtaining the best possible results, and I shall indicate how the burning may be carried on in the most rational manner.

Let us now consider the setting in the continuous kiln; in most cases the firing-shafts are arranged in such a manner that a straight flue is built up from the kiln floor to the fire-hole in the arch. On charging the coal into such a flue a little of it will be suspended here and there, but the largest part falls to the bottom. The necessity to distribute the coal has been evolved independently by practice and has been acknowledged to be necessary by all intelligent brickmakers. But this is ordinarily carried out in such a way that in the middle or in one or two

places of the shaft a so-called "cross" is allowed to project which offers resistance to the fall of the fuel, catches it and keeps it at a certain height in the kiln. Again, bricks are set in such a manner that they may be turned over when the parts of the kiln below them are burnt sufficiently; in this way the kiln floor is, so to speak, gradually raised. With this simple arrangement of the building in of "crosses," the trouble met with is that they either do not operate at all or too much. Either all of the fuel falls through and only a small part remains in position, or any accident causes an excess of fuel to be deposited at that place, and sometimes all of the fuel remains suspended on top. A proper distribution of fuel can be carried out only when sufficient space is allowed so that choking cannot occur in the flue, and when at the same time a continued resistance is offered to the falling of the fuel which prevents it from falling vertically and compels it to jump from one step to another. On each step but little fuel must be deposited so that no injurious accumulations nor choking take place. This is accomplished in such a manner that through every firing-shaft a lath (10 cm. wide and 1 to  $1\frac{1}{2}$  cm. thick) is placed, around which the firing-flue is built up as wide as the size of the brick will permit, in alternating courses, a brick being set close to the lath, once in front of it and again behind it. In this manner the firing-shafts are not only built up uniformly, making the conditions for the distribution and combustion of the coal in them everywhere the same, but they are also wide enough to avoid danger of choking, without however permitting the fuel to fall directly to the bottom. For the purpose of looking down to the floor of the kiln there remains a small or narrow slit corresponding to the thickness of the lath, which is to be removed after finishing the building up of every shaft.

When coal or any other fuel is thrown into such a firing-shaft, it can never fall directly to the bottom without striking several times and being distributed by the projected brick towards all sides. In some cases it is desirable to use a different arrangement; *i. e.*, when the highest possible temperatures are to be attained, and hence when a very large quantity of fuel

must be brought into the kiln. In this case, on charging the coal very heavily, there is always danger that the fuel does not burn away as rapidly in places as it should, and that hence the freshly charged coal rolls over the ignited coal and smothers the latter. In this case one must operate so that continuous pillars of fuel are put up in the kiln, but not so they reach down to the floor, because then the circulation of the air would be cut off from the lower flues. One proceeds in such a manner, especially for the burning of lime and cement, that the firing-shaft is made quite narrow in a place in the lower part of the kiln and then again widens. By throwing in larger lumps of coal one can close this shaft in the most narrow part and build up, so to speak, pillars of fuel, but at the same time one is enabled to allow so much of the ignited coal to drop to the bottom of the kiln as is necessary to produce the necessary heat at that place, by poking with a rod. With the predominating horizontal draft it is by no means necessary to charge much fuel at the kiln floor, because the flame is always directed towards the latter and is much stronger than is often desired. Another reason is that in the part of the kiln space being fired, which is next to the stack flue, the effect of the draft appears more strongly than in the other places by forcing the flame into the horizontal flue. Since here also the flame is directed towards the bottom, a direct charging of the coal to the floor is in many cases quite unnecessary and often only serves to stop the air circulation at that place.

The firing of the continuous kiln has often been considered the simplest form of direct gas-firing possible, but wrongly, for it has less in common with the latter than any grate furnace. All fuels on heating decompose at first into gaseous and in part combustible products (into steam, hydrocarbons, hydrogen), and the remaining carbon (charcoal, peat-coal, and coke). In gas-firing the coke produced in the first stage of gasification, on incomplete combustion with a limited introduction of air and with a thick layer of ignited coal, is changed to carbon monoxide, which then is burnt to carbon dioxide in another place. In grate furnaces the coke burns partially to carbon monoxide

and partially directly to carbon dioxide, according to the thickness of the layer and the intensity of the draft. In firing the continuous kiln the last condition just mentioned is the rule, since the conditions for the production of carbon monoxide, the main constituent of generator gas, are the most unfavorable possible, that is, spreading of the coal in thin layers and small quantities, lack of intimate contact between air and coal, and a large volume of air. It is true that the evolution of combustible gases takes place with great rapidity directly after firing, since the introduction of the fuel takes place in very small quantities and covers a large surface. This mode of firing does not cool the furnace surface to any extent. After the completion of this process the intensity of combustion is decreased very much and the remaining coke, whose quantity even with strongly bituminous coal amounts to 50 or 70 per cent by weight, burns only very sluggishly notwithstanding the hot air used for combustion. This appears from the fact that it does not assume an appreciably higher temperature than the remaining contents of the kiln; at least the coke never shows such a bright heat as may be observed on a grate of a furnace supplied with cold air, where in consequence of the intimate contact between air and coal the combustion is always much more energetic. This sluggish combustion of the coke residue of the kiln, which every practical man has observed, especially in the firing-shafts that are dying out, explains, on the one hand, that in spite of heavy charging, the intensity of the heat is at times decreased in the continuous kiln, and even the fire may go out entirely, and that the accumulation of the unburnt coal sometimes in large quantity is not a very rare occurrence; on the other hand, it explains that a large quantity of atmospheric oxygen always passes through the kiln without being used in combustion. It also affords an explanation of the fact that dark smoke can hardly ever be observed in the stacks of the continuous kiln.

The air drawing through the kiln, progressing from one fire-shaft to the other, is gradually robbed of its oxygen; but this never takes place completely, since only the volatile constituents of the fuel burn easily. The remaining coke behaves quite

indifferently in regard to combustion on account of the insufficient contact with air, so that it is not enabled to remove all of the oxygen of the air. Direct investigation has shown this; and if this is true concerning the air after it has passed all the firing-flues charged with coal, it is also true in a still greater measure in the middle and back parts of the kiln space.

In a previous communication I have discussed the course of combustion in a continuous kiln in which the conditions were especially favorable for a complete consumption of the oxygen, inasmuch as large quantities of fuel were charged at one time in opposition to the practice customary in the burning of brick. These investigations in regard to the nature of the products of combustion were undertaken in a continuous kiln used for the burning of lime. It was found that the fire-gases taken from the parts of the kiln which were at a low heat were almost entirely robbed of their oxygen only after the charging of fresh fuel, and the content of oxygen increased very strongly after the burning down of the fire; hence half up to two-thirds of the latter passed the kiln unconsumed. An excess of combustible gases especially of carbon monoxide was not observed at all. Further investigations in a continuous brick kiln have shown that in a kiln with a moderate draft only one-quarter to one-third, and with a weak draft and directly after firing only half, of the oxygen brought into the kiln was really used for combustion. For this reason the fire-gases in the usual mode of burning must be designated as being strongly oxidizing. The condition of the kiln gases in the continuous kiln is oxidizing even when, after thorough ignition of the fuel, the draft is completely shut off, inasmuch as the coke contained in the kiln is not able to remove all the oxygen from the weak stream of air which under these circumstances flows in at the kiln floor and again draws back in the space beneath the arch. Only in the immediate vicinity of the firing-shaft is it possible for reducing gases to be active within a small space directly after charging the fuel, and this explains most of the discoloration of the ware close to the firing-shaft.

While in all other kiln constructions an excess of combusti-

ble gases in the kiln gases alternates with an excess of oxygen, this change being recognized by a periodic more or less strong smoking, in the interior of the continuous kiln there is present on an average an excess of oxygen, and only within a very narrow space and with strongly flaming fuel can the effect of reducing influences be prominent.

Valuable as the ordinary method of firing the continuous kiln is for producing smokeless combustion, and great as the economic advantages offered by it are, still owing to this very fact it offers greater difficulties in the production of uniform colors than is the case in other kilns.

The observant reader of the discussions concerning the effect of the separate constituents of the fire-gases upon the clay and the color phenomena, will readily notice what an important rôle the periodically appearing reducing influences exert upon color; and that especially in the use of fuel containing sulphur, which applies to coal and lignite, in almost every case the reducing gases are the factor which renders harmless the injurious influence produced by the presence of sulphur compounds. The reducing gases are also capable of removing discolorations already produced, and in the case of light-burning clays low in iron they prevent the appearance of discolorations due to free iron oxide. In the continuous kiln the reducing influences are almost eliminated, or make themselves felt only locally in the neighborhood of the firing-shafts, and for this reason permit the discolorations, due to the presence of sulphur with the always simultaneous presence of excess of oxygen, in a greater measure than smoking kilns. It is thus shown that the presence of smoke in the kilns of the ceramic industry has a certain justification and often is absolutely necessary in order to produce the desired colors.

This explains the technical difficulties which are offered in the use of the continuous kiln for many branches of the clay industry, especially in the manufacture of terra cotta. It is now necessary after knowing the cause of the evil to find ways and means to render the scientific results of practical use. We would thus make for the continuous kiln a larger sphere of use.

fulness, which it well deserves on account of its economic advantages, so that finally it will be possible to make use of this kiln with a greater assurance of success, than was the case up to the present, for the manufacturer of such products for which a pure and uniform color is demanded.

The technologist or manufacturer who is desirous of producing better products in the continuous kiln than the average products burnt with the usual method of operation, will first be compelled to explain the possible causes of the different coloring phenomena which so far have offered the greatest difficulty in this kiln. Of course an extensive study is necessary, on account of the variety of factors to be taken into consideration, and it will not be given every one to overcome the difficulties met in the light of correct knowledge and without scientific help. This is the point in which scientific education is often insufficient and where practical experience can lead only to an uncertain groping, while observation trained in the field of scientific principles can alone lead to the proper knowledge.

As everything in nature is subjected to definite laws and nothing is due to accident, so also are the colorations of clay subject to definite laws. It will be necessary to determine clearly whether certain colors are really the result of the action of the fire alone, or whether they are to be traced to the drying and water-smoking process ; it will be necessary to determine whether discoloration has been produced by the efflorescence of salts from the clay itself, by fusion in it, or by the deposition of ash and condensation due to water-smoking ; it will be necessary to know what colors the clay assumes under the influence of reducing or oxidizing gases at the different temperatures, under the simultaneous presence or absence of sulphur compounds, and what shades of color are to be attributed to the condensation of the body due to vitrification.

Accordingly, a decision will have to be made in regard to what fuel is to be chosen, whether one containing sulphur, or free from sulphur, whether one rich in gas, making a long flame, or one low in gas, making a short flame, whether it may be used wet or dry, whether it is necessary to so set the

ware that much or little fuel can be stored in the firing-shaft, whether it is necessary to burn with a lively or slow draft, whether the smoking of the chimney is to be considered a fault or a deficiency in burning, etc. With the great variety in the properties of clay it appears impossible to obtain a definite rule concerning the operation of a continuous kiln in which products of a higher grade are to be produced, and it appears to me to be a mistake to formulate definite prescriptions and so-called practical experiences which in a special case may be very impractical.

For this reason I must deny myself the discussion of all possible cases which might only confuse the reader. I will restrict myself to showing in a concrete case, which however often returns in practice, what path is to be followed.

Mr. E. in H. had built a continuous kiln in 1875, in order to better meet competition of neighboring brickyards favored by local circumstances, by saving fuel in burning. Inquiries and test burns in other continuous kilns appeared to show with certainty that the product, yellow front and face-brick, could be burned in a continuous kiln in the same quality which was turned out by the old kilns. The continuous kiln was built and, with the help of a so-called instruction burner, put in operation; but the bricks in this kiln were not of a yellow color, but showed all colors, green, yellow, and reddish brown; though they were harder and more uniform in regard to hardness, they showed colors which they had never shown in the old arched kilns.

The first failure was excused with the newness of the kiln and the moisture, and it was hoped for better results. The water-smoking was done with refined care, and yet in vain. The result remained the same, the hope for improvement became constantly smaller, and experiments of all sorts were made till nobody had a clear conception of anything. One chamber furnished a few hundred, the next a few thousand bricks of the desired color; it was believed that the secret had been unraveled, but further work produced nothing.

The Gothic-shaped brick, for obvious reasons, could not even be used for common brick, and rapid burns in the old kilns had to be made in order to fill the contracts. All suggestions did

not help. The storage space was filled with rejected ware, the proprietor continued to become more discouraged, the foremen smarter day by day, the workmen lazier and more exasperating, and in addition the competing firms made sarcastic remarks, the whole forming a picture which many a reader will clearly appreciate from actual experience.

The phenomena pointed distinctly to the fact that one dealt here with the coloration of a marl clay by volatile sulphur compounds in an oxidizing fire. In the old arch kilns the clay had assumed a straw-yellow to a light green color, with the exception of the top courses, which appeared flashed with a strong red, and showed a white coating at the covered places; fused black points, originating from grains of iron sulphide, did not admit of any doubt in regard to the action of strongly reducing fire-gases in the old kiln.

In the continuous kiln the color of the very hard burned brick at the fracture was not yellowish or yellowish green, but reddish or brownish yellow; the surface of the portions exposed in the kiln were spotted more or less, red to reddish brown, on the covered places as well as the interior of the brick; the iron sulphide grains had not fused into black points of slag, but formed a loose red powder of iron oxide, thus indicating an oxidizing fire. In the erroneous supposition that the smoke was the cause of the various colors, the air was admitted for the purpose of burning it completely by loosening the firing-covers during the pre-heating of the kiln.

Only in the immediate vicinity of the firing-shaft, where the brick had come in direct contact with the coal or where they were touched by the yellow flame, the brick showed the desired straw color. The phenomena observed at the continuous kiln, as well as on the products of the old kiln, left no doubt in regard to the remedy to be followed according to the scientific determinations which were previously discussed in connection with the example of the Birkenwerder marl clay. The reddish color of the clay was produced by the lack and even the careful avoidance of a reducing kiln atmosphere; the red-brown flash

was to be explained by the same cause and the sulphurous acid originating from the fuel.

In order to remove both difficulties it was only necessary to fill the kiln space periodically with a strongly gaseous, that is, smoky atmosphere. For this purpose all the dampers of the kiln were closed, but firing with coal was continued, using larger quantities of coal than had been customary in the ordinary burning. In consequence, the entire kiln was filled with a thick black smoke which was allowed to draw off through one or two open rows of fire-holes in the cooling part as far as it showed a distinct red heat, in order to avoid a deposition of soot, that is, a blackening of the kiln chambers that were being cooled. The evolution of sulphuric acid due to this treatment with smoke was so intense that it was almost impossible to stay on top of the kiln, and another problem still remained, that of properly disposing of injurious fumes. The charging of coal was repeated as soon as the kiln atmosphere again had become transparent in the firing-holes.

After the action of the smoke had been continued for three-quarters of an hour to an hour, the ordinary mode of burning was again resumed, and the same procedure was repeated at intervals of eight hours. As the theoretical considerations indicated, the success was a complete one. The color of the brick throughout the entire kiln was the required normal yellow color even in the interior, a color which so far had been obtained only in the firing-shaft; the reddish brown flashes and spots had disappeared and the kiln to-day furnishes face-bricks as good and as uniformly colored as they have been obtained in the old kilns, with a great decrease in the cost of burning and much less waste.

As was done in this case, the difficulties met with in other cases may often be removed in some very simple manner, although the method chosen in this example will not always prove suitable. It is only necessary to follow up the causes of phenomena.

## Notes on the Theory of Firing the Continuous Kiln

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Supplementary to the discussion of the question "Which is the better method of firing the continuous kiln, firing at definite intervals of time accordingly as the coal burns, that is, about every fifteen to twenty-five minutes, charging all of the firing-holes at once, or firing every five to eight minutes, jumping two rows of firing-holes, and firing only one-third of them at the same time?" Mr. W. Olschewsky, in the *Deutsche Toepfer und Zieglер Zeitung*, presents some communications in which he treats of observations regarding the composition of the fire-gases according to the methods of firing indicated above. The compositions of the fire-gases communicated in his article represent samples which were taken  $\frac{1}{2}$ , 1, and  $1\frac{1}{2}$  meters under the crown of the arch of the second chamber, at a low red heat, all fire-holes being charged at intervals of twenty-five to thirty minutes and are reproduced in the following table:

Number of test.	Depth of taking sam- ple below the arch. Meters.	Composition of the fire-gases.				Time after firing in minutes.
		Carbon dioxide.	Oxygen.	Carbon monoxide.	Nitrogen.	
1	0.50	12.2	8.2	0	79.6	1
2	0.50	9.0	11.2	0	79.8	5
3	0.50	5.6	14.9	0	79.5	11
4	0.50	4.6	15.7	0	79.7	23
5	0.50	11.4	8.9	0	79.7	2
6	1.00	8.8	11.6	0	79.6	5
7	1.00	5.3	15.1	0	79.6	13
8	1.00	12.0	8.9	0	79.1	1
9	1.00	9.0	11.4	0	79.6	5
10	1.00	5.2	15.2	0	79.6	10
11	1.00	5.0	15.6	0	79.4	16
12	1.00	3.6	17.0	0	79.4	31
13	1.50	10.5	9.8	0	79.7	2
14	1.50	5.4	14.9	0	79.7	7
15	1.50	4.2	16.2	0	79.6	12
16	1.50	4.6	15.7	0	79.7	22
17	1.50	4.0	16.2	0	79.8	28

The course of combustion can best be followed by observing the amount of free oxygen shown in the columns. Since the atmospheric air contains 21 per cent by volume of oxygen, and since from one volume of oxygen on combustion one volume of carbon dioxide is produced, the approximate per cent of air passing through the kiln unused can be calculated. This percentage, in the most favorable case, immediately after charging all the fire-holes, is 39.1 per cent; this is nearly one-third. In the most unfavorable, after the burning down of the fuel, it is 81.9 per cent, or above four-fifths. The average of all observations is 62.9 per cent, or roughly two-thirds. In other words in the case observed there passes through the kiln, on the average, three times as much atmospheric air as would be theoretically required for the most economical combustion. This is by no means a favorable proportion which, however, is balanced by other advantages, *i. e.*, the utilization of the heat from the cooling brick and the waste gases, which results in an actually economic mode of burning.

In firing one row of feed holes at intervals of from two to three minutes, the per cent of carbon dioxide contained in the fire-gases amounted to 6.5, 6.9, 6.7, 6.9, and 7 per cent, thus averaging 6.8 per cent, which approaches the content of carbon dioxide of the preceding test whose average is 7 per cent; thus also in this case three times the amount of air required for theoretical combustion passed through the kiln and the difference in both cases is only that, as was to be expected, in the first case a fluctuation around the average value is observed.

Hence, in regard to the pyrometric effect of combustion, both methods may in general be considered as being equivalent, except when, owing to the composition of the fuel used, the fluctuations in the composition of the fire-gases in the first case are so wide that the oxygen of the air disappears immediately after a heavy charge of fuel, its place being taken by unburnt combustible gases. This case, as I have already shown in a previous article, will occur the sooner, the more readily larger quantities of volatile products are evolved by the coal; that is, the easier the coal flames.

According to his experiments Olschewsky, however, believes

that the method of firing in very short intervals must be preferred for the reason that with the greater fluctuation in the composition of the fire-gases, coincident with the first method of firing, a wide fluctuation of temperature must go hand in hand, thus causing fusions quite readily when the temperature has almost reached the melting-point of the clay. Such an assumption can not be justified, neither theoretically nor practically. It stands in contradiction to the experience in the old periodic brick kilns in which the fluctuations, in regard to the constitution and temperature of the fire-gases, are of necessity wider both as to magnitude and time. The increase of temperature can never extend, according to the table given, beyond the time of a few minutes, and at most can exert an influence only upon the outer surface of the brick, while the interior remains unaffected. If such an influence should be considered of determining importance (which I do not consider justified), it would tend to be a favorable rather than an injurious influence upon the quality of the ware, inasmuch as it would promote the vitrification of the surface retaining as much as possible the exterior shape. This will be true in a still greater measure the farther the point of incipient softening is removed from that of complete fusion, points which with many materials are very far apart. The view of Mr. Olschewsky, however, contradicts the practice of burning vitrified brick, which consists essentially in bringing the temperature of the surface of the brick, by firing as energetically as possible, rapidly to the melting-point of the clay, and then allowing the temperature to fall slightly by allowing the fire to burn down, in order not to put the refractoriness of the clay to too high a test.

But if really a theoretical advantage of firing in the short intervals of about five minutes could be proved, there is still to be considered the practical point of view which is opposed to the carrying out of this plan; this is the strength of the burner which does not permit him to fire in short intervals of five minutes, and at the same time observe the progress of the burn.

## **Calcium Carbonate in Clay, and its Influence on the Properties of the Latter, with Special Regard to the Manu- facture of Front Brick**

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W. H. ZIMMER, PH.D., TRANSLATOR

Calcium carbonate is the most frequently occurring, and the most important for manufacturing purposes, of the admixtures that are contained in the ordinary potters' and brick clay, and which were incorporated with the latter during the natural washing process, to which the clay owes its origin. Rocks, free from lime, which, through weathering and transportation by water, are changed into clay, will naturally result, first, in a clay free from lime; however, before the latter is deposited from the water, it has many opportunities for mixing with calcareous materials. Along rivers, or at the mouths of rivers, the deposits do not only contain pure clayey mud, but also the weathering and erosion deposits of calcareous rocks and calcareous mountains, so that the deposition of these materials occurs simultaneously. Besides, fresh water, as well as the sea, is the dwelling place of shells and other animals, and also of billions of microscopic animals of great variety, whose calcareous shells, taken from the lime salts of the water, sink to the bottom simultaneously with the clay mud of rivers, swamps, lakes, and oceans. In this manner, there is added to the clay not only a very considerable amount of lime, but conditions are favorable for the formation of great deposits of pure calcium carbonate (soft limestone, chalk, etc.). The lime contained in clays is chemically combined with silica and alumina only to a slight extent. For the most part, it is present as calcium carbonate mechanically admixed, and its presence can easily be detected, even by the layman, by pouring on the clay an acid, like sulphuric acid, hydrochloric acid, or strong vinegar, when a strong effervescence will indicate the presence of calcium carbonate.

The view is held by many that clays which effervesce strongly on contact with acid, and hence possess a considerable

content of calcium carbonate, are unsuitable for the manufacture of bricks. However, this is by no means always the case. When the calcium carbonate is present in moderate quantities, and in a suitable, finely divided state, it is often a very welcome constituent of the clay, since in burning it promotes vitrification; but, on the other hand, when the calcium carbonate appears in the shape of larger, solid pieces, that is, as residue of limestone or chalk, or concretions of all sizes and shapes which are produced especially in the upper layers of the clay deposits, by the cracking of the latter, or through the penetration of roots and the flow of water into the channels thus produced, then the clay becomes entirely unsuitable for all the purposes of brick-making, except it be washed. This is quite frequently true even when the grains of calcium carbonate are so small that they can hardly be recognized as such with the naked eye. However, if this compound of lime contained in the clay is so finely divided that the small particles cannot be distinguished from the rest of the clay mass with the naked eye nor can be separated by washing, then it will not, in general, exert an injurious influence upon the clay except when it is present in very large quantities. For this reason, when speaking of calcareous clays, we will always understand only such as contain the calcium carbonate in a state of fine division, so that it will cause no spalling of the ware after burning. As the most extreme limit for the content of calcium carbonate in clay, when considering the production of weather-proof building material, may be taken a content of 25 per cent, provided the ware is well burned. Occasionally, clays with 30 to 33 per cent are used, but if the content of calcium carbonate exceeds this, the products burned from such clays will always have a great tendency to disintegrate and to form whitewash. This has been noticed with a much smaller content of lime whenever the temperature of burning was not carried at least to the beginning of vitrification. Although in this matter other factors play an important rôle, it may be said that in general those brick clays which possess an appreciable content of calcium carbonate, especially when soft burned, are more subject to the destructive agencies of the atmosphere than those free from

lime. This experience explains why the red burning clays, either free from or very low in calcium carbonate, are used for weather-resistant products, as roofing-tile, while the clays high in this compound, ordinarily burning to a yellow color, are usually entirely unsuited for this purpose.

The property of calcareous clays, to be in general less resistant to the weather, is partially counterbalanced in practice by the fact that they do not possess a very high melting-point, and hence are easily brought to that degree of vitrification with which they are sufficiently resistant to the effects of the weather.

Such a high content of calcium carbonate as is shown by a large number of deposits of the North German plains and the coasts of the Baltic and German Sea (from 20 to 25 per cent), gives to the clay many useful properties, although it causes, as we will see later on, great difficulties in the process of manufacture. Since the finely divided calcium carbonate is not a plastic substance, the clays with a naturally high content of it, even when very fine grained, owing to natural or artificial washing, are usually not too plastic as a brick material, and hence, in most cases they require no further additions of non-plastic constituents. Nearly always they take up water easily. They require comparatively little water for the production of a mass sufficiently plastic for working, and in consequence of this, they shrink but little in drying and have but little tendency to crack; these properties are all to be ascribed to the finely powdered calcium carbonate.

Investigations which we made several years ago for members of the German Clay Workers' Association, who worked their clays with machines, showed that the clays in question can be worked into a bar with a content of from 20 to 24 per cent of water, in terms of the dry substance, while the clays of the lignite formation, low in lime, and the more recent ferruginous clays, usually required 25 to 30 per cent of water in order to soften to a similar plastic mass, and hence possessed a correspondingly greater shrinkage.

Since the calcareous clays, on burning, not only lose the chemically combined water of the clay, but also the carbon diox-

ide, amounting to 44 per cent of the calcium carbonate contained in them, the brick made from such products will be the lighter and more porous, the greater the content of lime. At the same time, these clays show but a very small shrinkage up to the temperature at which softening occurs, owing to incipient fusion. From this point on, the mass liquefies very rapidly and loses its shape; hence it is more difficult than with other clays, to produce straight and sharp vitrified brick, porcelain-like throughout the mass. These, when once produced, are extremely resistant to the influence of the weather. The clays do not stand in the fire, in technical parlance; this means, scientifically expressed, that the temperature at which the softening, the closing of the pores, and the formation of a porcelain-like, dense mass takes place, and that at which the clay liquefies completely, lie rather close together. In general, more experience is required than for other less rapidly softening clays, to avoid fusion (that is, to produce good, straight and sharp-edged bricks). This circumstance makes the manufacture of weather-resisting brick from calcareous clays very difficult, and hence it is often necessary, in order to keep within the required shapes, to work with temperatures that, though giving to the brick the characteristic yellow color which indicates the vitrification of the lime with the other constituents, does not do away with the earthy, strongly absorbent fracture. Products of this kind, often and erroneously called face clinkers, form the main contingent of the light-colored brick material used in Northern Germany for facing fronts, although their great porosity makes them very unsuitable for this purpose. When not properly burned, on account of a peculiar brittleness inherent in calcareous bodies, they offer but little resistance to the northern climate. Besides this, they soon become gray and black, owing to the strong absorption of water, dust, and soot floating in the air; or surface discoloration is caused by the growth of low plant vegetation, microscopic organisms, etc., giving rise to yellowish green or bluish green discolorations. These are defects which can be avoided only by hard burning, so that the product becomes quite dense; this, however, with very calcareous clays, is practically not possible.

without a very great decrease in volume and a great change in shape connected with this, at least for the purposes of unplastered buildings.

When the extensive deposits of calcareous clays of the North German plain are mentioned as a specially suitable material for the manufacture of clinkers (the German and English term for vitrified paving brick), and the hope is thus expressed that clinkers might be used more in our buildings, exposed as they are to a northern climate, this might, at first sight, appear as a correct statement. However, on examining the peculiarities of the raw materials more closely it will be found that the limited use of clinkers in building is not only due to the oft-mentioned lack of understanding on the part of the architects and builders and the lack of technical knowledge on the part of the brickmaker, but is largely due to the difficulties offered by the clays. These difficulties make it impossible, for obvious commercial reasons, to raise the burning temperature higher than is necessary to give to the brick the hardness required for transportation and use.

It is true that a content of lime in a clay is an especially good means of promoting glassy combinations in burning, which, so to speak, penetrate the clay mass and make it resistant to the action of atmospheric attacks. However, one must never forget that the calcium carbonate does not only give to the clay the useful lime but, with the latter, also carbon dioxide. It is the neglect of this consideration which gives rise to many futile practical attempts. Clinker materials, whose good quality has been recognized (for instance, the Oldenburg products and those of Schwarzehuette, which aroused the interest of all experts at the Berlin Building Exposition), lose on burning only 3 to 4 per cent of chemically combined water, which leaves pore spaces that, at a sufficiently high temperature, are filled out without an appreciable change in volume, leaving a perfectly dense mass. In these, the cementing is produced by fragments of easily fusible minerals, while, on the other hand, the content of lime is to give rise only to the formation of very fusible silicates. In the calcareous clays, the loss in weight is much more; in those which,

in consequence of their content of lime, assume a yellow and later on a green color, it is seldom less than 12 per cent of the dry weight, often even 16 to 18 per cent, due to the chemically combined water and carbon dioxide. Without causing a considerable shrinkage at a moderate temperature, these volatile constituents first produce a looseness of structure and porosity; on heating the clay up to softening, the spaces produced by the removal of the volatile constituents must be filled out, and if these spaces represent a large volume, this can only take place under a corresponding decrease of the external dimensions. If, for this reason, the burning temperature is to be raised to a point at which a brick material is produced, which is resistant to all attacks of the weather, the changes in volume in very calcareous clays are so large and the practical difficulties so great that, owing to this reason alone, the use of the material for building-brick must be given up. If really weather-resisting products are to be obtained from calcareous materials, the content of lime, owing to the great shrinkage in burning connected with it, must not exceed a certain limit. It will not be far amiss to consider as the maximum permissible amount, a content of 12 to 15 per cent of calcium carbonate, a quantity which is hardly sufficient with many clays, especially those high in iron, to produce the desired yellow, or yellowish green color of the brick; but this content of lime is often exceeded in order to produce the yellowish green color, to the disadvantage of the weather-resisting power.

Another peculiarity of the calcium carbonate which is to be especially considered in the manufacture of face-brick and terra cotta, is the one already indicated, of imparting to ordinary brick clays a yellow or yellowish green color. This color, like the ordinary red color of the clay, is to be ascribed to the never-lacking content of iron oxide. In brick clays free from lime, the iron oxide, according to its quantity and the intensity of the burning temperature, produces a pale to dark red color; if such a clay is blended with calcium carbonate by washing, after adding a sufficient quantity, a yellow burning clay will be produced. According to direct experiments, this yellow coloration appears most distinctly when the clay contains, for 1 per cent of iron

oxide, at least 3 to 3.5 per cent of calcium carbonate. The yellow coloration appears at the lower burning temperatures and grows constantly brighter the more the content of calcium carbonate exceeds this minimum. It is produced only at the higher temperatures and becomes the darker, changing to yellowish red or yellowish brown the more the lime approaches the given ratio. If the content of lime is low, it may be capable of changing the red color of the clay; but it will not be possible to produce a pure yellow color in burning and there results the indifferent, undesirable blending of colors shown by most of the ordinary bricks which are entirely unsuitable for facing buildings.

From this it appears that the main purpose of the manufacture of face-bricks, which is so often solely the production of pure colors, is readily attained only with clays in which the lime is either entirely lacking, or its content is so low that it can not exert an essential influence upon the red color of the iron oxide, or when it is so large that the red color is readily changed to yellow. That the latter extreme tempts the manufacturer only too readily, in many cases, to neglect the conditions of the highest possible weather-resisting power, has already been indicated above.

When I made the statement that the yellow color is produced with ease only with as high a content of lime in the clay as possible, I did not mean that the same result could not be attained (to a certain degree, using special precautions), with clays containing but a moderate content of lime, which I have designated as being the most desirable for the manufacture of clinkers under the existing conditions. The discussion of this question, to which but little attention has been paid, will be reserved for a further communication.

## Note on Brick Colors

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W. H. ZIMMER, PH.D., TRANSLATOR

The appearance of red discolorations on yellow bricks is a phenomenon which is not an infrequent one to the sorrow of the manufacturer. I have in my possession, two yellow bricks, the one having come from the brickyard of Mr. Hecht, in Neuhof near Stralsund, the other from Szegedin, in Hungary. Both show a red crust on the surface. The phenomenon in this case took place to such a depth, that it is possible to collect a sufficient quantity of the material and to determine, by analysis, the cause of the trouble. Samples of the crust and of the yellow core were examined, and from the difference in the composition of the crust and the core the cause of the difference in color has been determined. Before I begin to explain the phenomenon, I shall consider briefly the conditions which cause the coloration of the burned clay. On examining a clay analysis, one finds mentioned nearly always the same constituents : silica, alumina, iron oxide, lime, magnesia, potash, soda, sulphuric acid, carbon dioxide, small quantities of manganese, and of phosphoric acid and water. These ingredients must be made responsible for the coloration of the clay products, unless it is produced artificially through the addition of different metallic oxides, as the oxides of chromium, uranium, manganese, copper, etc. When only the constituents naturally belonging to clay are considered, of the entire series of ingredients mentioned, only the iron oxide can be made responsible for the many variations in color shown by the burned clay products. It is known that the color goes through all the variations from white through yellow, orange, red, blue, brown, up to black ; all these colors are produced by the combinations of iron. This might appear wonderful ; we are accustomed so much to look for a definite effect from a definite cause that it appears almost incredible, when we at once ascribe to a single ingredient the most varied

effects in color. In proof of this statement I want to call attention to the pure kaolins ; these, after burning, possess a white color, as we find it in porcelain. The ordinary bricks possess a red color ; but there are also yellow bricks in many variations. I have explained, previously, how the blue paving tiles are manufactured in Holland, and I have traced the color back to the iron. At present I am working with a clay from Ziesar, which is used there as a slip glaze for a refractory clay, one which is rather high in iron, and which, when burned over the Bunsen burner, produces a red color. When I heated this clay stronger over a blast-lamp till it fused, it showed a blue color. The glaze of the pottery for which it is used is yellowish brown. The same substances can thus produce, at one time a red, a blue, and again a yellow color. When it is said that all these colors are caused by the same substance, one is reminded of the magician who pours from the same bottle, red or white wine ; still there exists here a definite law, and the chemist is right when he says that all these colors are caused by the compounds of iron.

The iron has different degrees of oxidation ; namely, the ferrous oxide, the ferric oxide, and standing between both the ferroso-ferric oxide. Who has not seen iron-rust ? It is a compound of iron oxide and water. Neglecting the content of water, there are contained in it, 28 parts of iron and 12 parts, by weight, of oxygen. The ferrous oxide is less known because it is not ordinarily found in nature. It consists of 28 parts of iron and 8 parts of oxygen, and between both there is the ferroso-ferric oxide, which consists of 28 parts of iron and 10 parts, by weight, of oxygen. These different oxides form with silica quite differently colored compounds. In this manner the ferric oxide produces especially the yellow and the red colors, the ferrous, the blue and green, those of the ferroso-ferric oxide being between these limits. According to the mixtures of these oxides the most variously blended colors are produced.

In regard to the other ingredients contained in clay, the manganese alone need be considered, it giving rise to a brown color. Since it exists in a clay only in very small quantities,

together with the iron, we may neglect completely the effect of the manganese; it tends to produce only shades or tints. All the other substances contained in clay are not coloring in themselves, but they may play a rôle, in so far as they influence the effect of the iron compounds. Lime, especially, is capable of completely neutralizing the coloring effect of iron. Many insist that magnesia does the same but sufficient experiments in regard to this have not yet been made. In explaining the phenomenon of red flash on yellow brick, the lime plays an important part. It is known that when a yellow burning clay is heated to the temperature which suffices to expel the chemically combined water, the clay assumes a red color; when the temperature is raised, the color changes through white into yellow and orange till finally, on vitrification, the color becomes green.

If we now ask how it is possible that the red color due to the iron is neutralized by the lime, the investigations concerning this point have not yet afforded a perfectly definite conclusion. Prof. Remelé thinks that a double silicate of iron and lime is colorless; but it could also be assumed that another combination is formed in this yellow brick clay, analogous to the coloring constituent of the cement. This, though not proved, has been made quite probable through the investigations of Dr. Michaelis, who endeavored to show that the coloring substance in Portland cement is a combination of iron oxide and lime. This compound is olive-green. If thus, the heat of the kiln is sufficient to render the lime active, this compound will be easily formed.

If the question be asked, why, with a green coloring combination, a white stage of color could exist, the following might serve as an explanation. If one considers that the red becomes gradually pale and turns to green, and that, as is well known, green and pink are complementary colors (that is, when blended produce white), it appears plausible that the transformation stage is white, and that the green color appears more distinctly only at a higher heat. All of the lime has become active and the last trace of red has disappeared, and only the green color of the iron oxide compound is visible.

This matter is not definitely settled, but so much is known that in order to take away the coloring power from a definite quantity of iron oxide, a definite per cent of lime must be present in the clay. It can be said that for from 4 to 5 per cent of the iron oxide in a clay, about 10 per cent of calcium carbonate is required in order to do away with the red color. We might ask, now: How is it possible that with a yellow burning clay which has been exposed to the temperature necessary to produce the iron lime silicate, or the iron lime compound, a red color can again appear on the surface? The analyses of the brick mentioned above have shown that the yellow core from the brick from Neuhof contains 0.5 per cent of sulphuric acid, while the red crust contains 9 per cent of it. The other brick from Szegedin shows this difference between core and crust still more strikingly. While the core contains about 0.75 per cent of sulphuric acid, the content of sulphuric acid in the crust has increased to almost 20 per cent.

This is highly interesting. To the chemist it appears at once, that in this case the red color is bound to appear again, since sulphuric acid and lime together form calcium sulphate, and the temperature which is used in burning the brick to a yellow color is not high enough to decompose the sulphate. The lime, having been fixed by the sulphuric acid and rendered inert for the further chemical processes at this temperature, can only be considered as a neutral, non-plastic material.

The lime cannot enter into chemical combination with the iron, since it is bound by sulphuric acid. Hence the red color of the iron must again come into prominence. The fact that the sulphuric acid exists in the crust can hardly be explained in any other way but that it has come from the fuel. This takes place in all brickyards and cannot be attributed to any accidental causes. It is known that nearly all fuel contains sulphur, especially coal. The content of iron sulphide in coal, which is the real source of the sulphuric acid, is sometimes considerable, so there can be no doubt that large quantities of sulphur can be taken from the fuel to the brick.

How can we avoid the admission of sulphuric acid and

with it the discoloration of our brick? The formation of sulphuric acid cannot take place when no water vapor is present; hence, attention is again to be given the water-smoking process. It is to be advised that the brick be set in the kiln as dry as possible, and that for water-smoking a fuel is used which contains little or no sulphur. If this is done the trouble cannot occur. First, sulphur dioxide is formed, which in this case exerts no influence; but when the sulphur dioxide can change to sulphur trioxide and then come in contact with water vapors, sulphuric acid is formed. Practical men frequently shrug their shoulders when speaking of the theoretical men, because the latter do not possess the knowledge of the routine work; but in this case it has been possible not only to determine by a simple analysis the cause of a phenomenon so troublesome to practice, but also to show a way in which discolorations may be avoided.

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### The Natural Colors and the Discolorations of Light-Colored Bricks

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W. H. ZIMMER, PH.D., TRANSLATOR

Where the problem to be met is the production of bricks which are to be used for the exterior facing of buildings, the fact must always be considered that their color must at least be within definite limits, not too far apart, and must be uniform within this range. Although a certain monotony in appearance is avoided when the separate bricks differ by slight shades, yet on considering the separate brick as a whole it must always be one color, and sharp contrasts are caused if the differences in shade, which are not pleasing to the eye, occur on one and the same brick.

For this reason the question, in regard (1) to the production of brick colors, (2) to the conditions under which discol-

orations and efflorescences are produced, and (3) to means of controlling the colors of the brick, has become such a burning one that it has given rise continually to extensive, but often fruitless and expensive, experiments with different kiln constructions, fuels, etc. Although the following observations and examinations are not exhaustive enough to give a complete answer in this direction, still they will serve to throw some light upon this topic, so little cultivated from the scientific standpoint, and to encourage further investigation and observation, which, as far as I am concerned, are far from complete.

The light-colored brick especially give the brickmaker great trouble in regard to body and surface colors, and for this reason they will be given particular consideration.

Although in the discussion of the causes of the brick colors we start from the interior of the brick, we must make a strict distinction between the following four phenomena which are deduced from very different processes:

First, the color of the body of the brick as observed at the fracture.

Second, the color of the brick body on or near the surface in so far as it differs from the color of the interior or the main mass.

Third, the coloring of the surface of the brick by foreign substances or by such that come from the interior during the drying, water-smoking, or burning ; that is, efflorescence, incrustations, etc.

Fourth, the coloring of the surface by foreign substances which form after the burning, during the time of storage, or after being walled up.

I. The clay substance in its purest state, having the ideal composition of the silicate of alumina and water (china clay or pipe clay comes nearest to this ideal), contains little or no coloring constituents, and hence, after burning, always appears as a white mass. Such a material, for obvious and important reasons, can not be considered with reference to the manufacture of brick, and with its cold white, could not satisfy esthetic requirements. However, all materials which

possess practical value for the manufacture of brick contain, besides the constituents named above, a number of others originating from the most varied classes of minerals, owing to weathering and mechanical disintegration. These give to the burned brick according to their kind or quantity often a very striking color, or exert some influence upon the surface color. These are especially the compounds of iron and manganese, and also of lime, magnesia, the alkalies, chlorine, and sulphuric acid or sulphur compounds.

Only the first two can be considered as the directly coloring constituents of all brick clays, since their compounds possess a pronounced color. Their colors vary greatly according to the quantity or to the simultaneous presence of other constituents, especially of lime, magnesia, and the alkalies, and finally the physical condition of the mass. On the other hand, the white-colored compounds of lime, magnesia, and the alkalies can only be considered in respect to color to the extent in which they influence the iron and manganese, while chlorine and sulphur compounds can solely be considered in regard to surface colorations, coatings, and efflorescence.

The colors which are produced by the compounds of iron run through all shades of green to black in the presence of ferrous compounds, from pink to dark red in the presence of ferric oxide, through all the shades of yellow in the presence of larger quantities of lime and very likely also magnesia. The manganese always accompanies the iron, but only in small quantities, and the colors of its oxides run through all the shades of brown and black.

It is known that the oxide of iron, which in the majority of cases must be considered the only coloring constituent, may produce a great variety of shades from yellowish red to violet-black, according to its state of division, and it will always assume a darker color when the clay is exposed to a high temperature. At a low temperature iron oxide, prepared from pure iron salts, like ferrous sulphate, has a bright red color. This color becomes darker with increasing temperature, and assumes a dark violet color when heated to the most intense white heat, which causes extreme condensation of the particles.

Accordingly, the fact that brick clays become darker the higher they are heated, may be due to this property of the iron oxide, a fact confirmed by practice, and the production of a certain color of the brick serves the practical man for judging the degree of burning.

The iron oxide retains this property of producing a red color, as long as the mass of the clay retains its earthy porous character, but on changing to a vitreous condition, or in fusion, the color turns to black, this being the color given to glass by larger quantities of iron.

The conditions are different, however, when the colorless clay substance, beside the iron oxide, contains calcium carbonate, as is frequently the case. The lime acts as a flux on heating and causes vitrification to take place much earlier than it would occur without the presence of lime. It forms a silicate which, beside the constituents of the clay, takes up the iron oxide and the lime, forming a combination which, with a certain proportion between lime and iron oxide, assumes a white or yellow color. This compound is produced only at incipient vitrification, and the coloring power of the iron oxide is destroyed only at this point, while it is still retained at a somewhat lower temperature. Hence, clays containing lime and iron, on soft burning, assume a red color imparted by the iron oxide. This color gradually disappears on continued heating, and finally changes through flesh color and white into a more or less intense yellow or yellowish green, which finally on complete vitrification turns into green or black. It is self-evident that a certain ratio must exist between the iron oxide and lime in order to destroy the red coloring power peculiar to the iron compound, and it is a matter of course that from the ordinary clay analysis nothing definite can be deduced in this respect.

For example, the clays from Freienwalde and Rudersdorf analyzed for the society in the laboratory of the Mining Academy, are not yet able to destroy the red coloring properties of the iron oxide, while in the clays from Neuhof, near Stralsund, this takes place. In this respect we find a gap in the examinations of clays carried out in the customary manner, and it must re-

main for the future to fill it. There must be a law in regard to the proportion in which the main factors of brick colors, iron and lime, must stand to each other in order to destroy the red color of the iron peculiar to and characteristic of it. If from a clay, which burns yellow in its natural constitution and contains iron and lime, we remove the latter by means of acid, the ordinary coloring power of iron again predominates; that is, the clay burns to a shade of red corresponding to its content of iron.

All detailed observations in regard to the influence of manganese as well as of magnesia, are likewise lacking, but these demand less of our interest, since these constituents occur in clays usually only in smaller quantities, and when they occur it is always in the presence of larger quantities of iron oxide or lime which predominate and hide any appreciable influence upon color which might be traced to magnesia or manganese.

With these factors apparently so simple, the entire wide range of brick colors is covered. If, however, one considers to what extent the coloring influences are in reality subjected to variations in regard (1) to the coloring ingredients, (2) to the physical condition of the mass, and (3) to the different degrees of heating, the great number of shades of color (neglecting all discolorations due to the deposition of ash and efflorescence) are explained sufficiently, though not exhaustively.

2. The fundamental outline given above, governing the coloration of brick, applies only to the interior of the brick since it is more or less removed from the chemical and physical influences during the operations to which the brick is subjected; hence, the shade of color is dependent solely upon the higher or lower temperature. Conditions in regard to color are different, however, near the surface; there oxidizing or reducing effects can take place more readily. All the substances which are taken up from the fire-gases are concentrated near the surface, and hence all sorts of colors are often blended, while the color in the interior shows a certain uniformity.

In order to explain the phenomena belonging to this category, we must distinguish between such colorations which have been produced in the *clay body itself* near the surface and such

which have been brought about by the *deposition* of a coating, possessing a different color, upon the clay body. The phenomena of the first kind are real discolorations, the latter efflorescences. These and allied discolorations are often erroneously taken for the first and are considered identical with them.

Discolorations on red bricks, caused by the chemical action of the fire-gases, appear in a less disturbing manner than is the case with light-colored, especially cream-colored bricks. These, owing to their color, are much more sensitive in this respect, and especially because the real clay substance, as well as the coloring iron oxide, are rather indifferent to the constituents of the fire-gases, on account of their chemical indifference. In this case the discolorations may, as a rule, be recognized by their appearance as a glaze-like coating caused by the absorption of alkaline vapors, or as a reduction of the iron oxide to black ferrous silicate. Matters, however, are different in the case of the lime contained in the cream-colored brick, which possesses a well-defined, energetic affinity to a few of the impurities always present in the fire-gases.

For this reason, discolorations, which are especially troublesome to the brickmaker, are found more frequently on light-colored than on red brick, and practice confirms this perfectly.

I have pointed out, on a different occasion,<sup>1</sup> the influence which constituents of the fire-gases exert upon the clay under special circumstances, especially during the water-smoking process, in order to show that in using generator gas in brick kilns, the same phenomena of discoloration must of necessity occur, which we fear so much in the direct firing with solid fuel and that those who imagine that with the use of gas the difficulties of the ordinary burning will at once be removed, are sadly in error..

The following investigation will confirm the earlier verdict by the most convincing proofs. .

Among the discolorations shown by light-colored brick, the most frequent are those which appear on the exposed surfaces

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<sup>1</sup> See "Notizblatt," 1872, page 165.

as red or reddish brown flashes, while the covered parts are yellow. Although these discolorations may be found on using any fuel, they appear most strongly with the use of coal as fuel, and for this reason it is often customary, especially in operating the continuous kiln, to avoid as much as possible the use of coal for the production of good, light-colored brick. A distinction must be made in this respect between the red colors produced by imperfect burning, which may be recognized by the fact that, if the brick has otherwise assumed a yellow color, they appear in the core of the brick, or in places which have been covered in the kiln, and such colors which have been caused through the influence of the fire-gases and can not be removed by even the strongest burning. Sometimes the two phenomena appear on the same brick, and in such a manner that it has a red core, the outer portions being yellow and the surface again red. The two kinds of red are due to different causes: the one in the interior is caused by the fact that the temperature was not high enough to destroy the color of the iron oxide by the formation of a lime silicate; the red on the outside, usually more intense, is due to a chemical combination of the lime which made it impossible for the latter to enter into the silicate formation mentioned.

The red discolorations of yellow brick appear on the fracture as a layer of the thickness of paper, or as much as 1 mm. deep, which is colored most intensely on the surface of the brick; sometimes a greater thickness is observed. An especially fine example of this kind, with a discolored layer as much as 5 mm. thick from the brickyard of Mr. Hecht at Neuhof, near Stralsund, offered me an opportunity to make a closer examination which really gave rise to a surprising result. The interior of the brick was colored a pure cream-white, the surface dark blood-red with a gradual shading to a lighter color towards the interior; the brick had been burned in a continuous kiln, the fuel having been English coal. Splinters were chipped off from the outside discolored layer and these, in so far as they were colored a strong red, were finely pulverized and subjected to analysis.

At the same time, using exactly the same method of analysis, the yellow interior of the brick was analyzed by Dr. Aron.

The analyses gave the following results:

	In the red part. Per cent.	In the yellow part. Per cent.
Silica - - - -	63.71	71.25
Alumina - - - -	9.81	8.60
Iron oxide - - - -	5.16	5.92
Lime - - - -	8.72	9.24
Magnesia - - - -	2.20	1.89
Sulphuric acid <sup>1</sup> - - - -	8.49	0.61
Manganese } - - - -	traces	traces
Chlorine }		
Alkalies - - - -	1.90	2.49
	100.00	100.00

The difference in the analyses with respect to the content of sulphuric acid is extremely striking and characteristic in the highest degree. The sulphuric acid is in both cases to be considered as being united with the lime, and since 40 parts, by weight, of the acid unite with 28 parts, by weight, of lime to form calcium sulphate, it would correspond to a content of 1.04 per cent of calcium sulphate in the yellow portion and 14.43 per cent in the red portion.

<sup>1</sup> It was not to be expected that the brick should have an exactly uniform percentage composition in all parts, since the fracture of the brick already showed that the mass was not perfectly homogeneous. However, subtracting the sulphuric acid present in the red part (8.49 per cent and 19.58 per cent, respectively, which for the largest part may have been taken up only during the burning) and calculating the balance in per cent, then the composition of the discolored layer would be:

	In the brick from Neuhoef. Per cent.	In brick from Szegedin. Per cent.
Silica - - - -	69.62	56.86
Alumina - - - -	10.72	12.83
Iron oxide - - - -	5.88	5.58
Lime - - - -	9.53	15.82
Magnesia - - - -	2.41	4.39
Manganese } - - - -	—	—
Chlorine }		
Alkalies and loss on heating -	2.14	2.78
	100.00	100.00

Reduced to this basis no essential deviations are shown from the analysis of the yellow portion.

Calculating the oxygen ratios between the lime<sup>1</sup> not united with the sulphuric acid (the combined lime not being considered in regard to the formation of silicates, since the calcium sulphate is not decomposed at the temperature at which the bricks are burned) and the oxygen of the iron oxide, it is found that the ratio of iron oxide to lime in the red part is 1 : 0.34, and in the yellow 1 : 1.58. Hence, there is present in the yellow part, referred to equal amounts of iron oxide, nearly five times as much lime for the formation of the yellow silicate.

If in a similar manner these ratios of the clays, whose analyses are given in the *Sprechsaal*, 1872, page 119, are calculated, it is found that in the clay of Mr. O. Oppenheimer at Ruedersdorf, which assumes a pale red color with a greater percentage content of iron, a ratio of 1 : 1.11 is found; in that of Mr. Kuhnheim, at Freienwalde, which burns to a dark-red, one of 1 : 0.35 is determined just as it was found in the case of the red-colored portion of the Nethof brick.

Another point of view of the phenomenon, no less characteristic, is furnished by the analysis of a brick from the Brick and Building Company of Szegedin. This brick consisted of a very porous light mass made from a lean and very fine clay, the interior being of a sulphur-yellow, the outside of an intense dark violet-red color. The discolored layer, nearly 10 mm. thick, is darkest on the outside and shades through red to yellow towards the inside. The analyses of the outer darkest portion and the yellow interior were as follows :

	In the red-violet portion. Per cent.	In the yellow portion. Per cent.
Silica - - - -	45.73	56.07
Alumina - - - -	10.22	14.02
Iron oxide - - - -	4.49	5.49
Lime - - - -	12.81	16.53
Magnesia - - - -	3.53	4.50
Sulphuric acid <sup>2</sup> - - - -	19.58	0.74
Alkalies and loss on heating - - - -	2.24	2.66
Water - - - -	1.40	0.39
	100.00	100.00

<sup>1</sup> This amounts to 1.78 per cent in the red portion, and to 8.61 per cent in the yellow portion.

<sup>2</sup> See note referring to preceding analysis.

The excessively high content of sulphuric acid in the discolored portion indicates here the same cause as in the case just discussed, only that the combination of the lime has progressed still farther. The amount of lime corresponding to 19.58 per cent of sulphuric acid for the formation of calcium sulphate is 13.70 per cent. Thus all the lime must be assumed to have united with the sulphuric acid and part of the magnesia (0.64 per cent) must have been changed to the sulphate likewise. In the yellow portion of the brick the ratio of the iron oxide to lime according to the comparison given above is 1 : 2.86, which is still more favorable for the destruction of the red color due to the iron oxide, than in the case of the Neuhof brick. The ratio in the discolored layer has been lowered to 1 : 0; that is, the lime has entirely lost its ability to influence the red coloring power of the iron by forming a lime-iron silicate, since it is entirely bound to the sulphuric acid.

If now we ask ourselves, whence comes this high content of sulphuric acid in the outside portion of the discolored brick? we will receive as an answer: from the fire-gases, for the bricks are exposed only to these during the red coloring process. All fuels, with the exception of wood, contain sulphur,—peat least, lignite more, coal<sup>1</sup> most; this is volatilized in burning in the form of sulphurous acid. Under favorable conditions this sulphurous acid, especially and perhaps exclusively during the water-smoking process, when opportunity is given to water vapors to condense on the surfaces of the brick under the simultaneous influence of the lime of the clay and the excess oxygen of the fire-gases, oxidizes to sulphuric acid and thus removes the lime from the possibility of forming a strongly basic yellow coloring iron-lime silicate, thus maintaining the original coloring-power of the iron.

3. Not to be mistaken for the discolorations just described, are those which form in the shape of white or gray coatings on the surface of the brick during the burning, but do not represent a coloration of the body proper, nor do they penetrate into the

<sup>1</sup> The content of iron sulphide in coal varies between 1 and 5 per cent, and 2 per cent may be taken as an average.

interior of the brick. In their formation the chemical properties of the clay are involved in a less degree than the physical. These coatings consist either of efflorescences of salt, produced during the drying or water-smoking which are fixed during the burning, owing to the decomposition of the salts, or of fine ashes which adhere to the surface of the brick.

The former are peculiar especially to plastic clays, and on careful observation, are frequently detected on the air-dry bricks, particularly along the edges. They occur more frequently on smooth and dense surfaces, and hence are found most often on repressed bricks and the smooth surfaces of machine-made bricks. On the other hand, they are found rarely on the rough surface of common brick molded with sand. Under the magnifying glass they appear as wart-like, usually white, segregations on the surface. Their origin is to be explained by the fact that the water which penetrates the clay, especially if the latter contains sulphuric acid or chlorine, holds in solution soluble salts which, on evaporation, are left behind as solids. If now the clay is lean and porous, this evaporation can take place not only from the surface, but also in the clay body itself, the segregated salts thus being distributed over a large surface. If, on the other hand, the surface of the brick is very dense, or as it occurs in careless water-smoking, if the pores on the surface are filled with water, preventing the air from penetrating into the interior by diffusion, then evaporation can take place only at the surface, and hence a deposition of the salts from the water can take place only here, while from the interior fresh water is continually drawn outward by virtue of capillary attraction.

Hence those impurities of the clay which give rise to the formation of soluble salts, will be especially injurious to the color of the surface; these are sulphuric acid (iron sulphide), chlorine, magnesia, and the alkalies.

Since in many cases these efflorescences are produced only in water-smoking, and only when water vapors condense upon the brick, they may often be prevented by conducting the water-smoking process very carefully.

Still not only the soluble salts contained in the clay, but also

those which are taken up from outside sources during the burning, may give rise to efflorescence, being collected by the moist surfaces of the brick in water-smoking.

The sulphuric acid affording an opportunity for the formation of this efflorescence, has already been mentioned; but frequently the alkalies are the cause of the trouble, being volatilized from the ash during the period of maximum temperature, and deposited again in the colder parts of the kiln. Often delicate white coatings are found on the covers of the fire-holes of continuous kilns and the heating pipes; such a deposit in the continuous lime kiln of Mr. Frederick Hoffmann, at Nordhafen, in Berlin, proved to be a mixture of sulphate of potash and soda, potassium chloride and sodium chloride.

From these efflorescences occurring most frequently, those due to fine ashes can be easily distinguished. While the former represent usually white segregations, appearing wart-like under the microscope, the latter are of a dark, usually gray or brown color, and are composed of small splintery grains. These particles of ash, when coming in contact during water-smoking with a moist surface of the brick, usually adhere to the latter, but in the case of dry ware they unite but loosely with the clay, and may even be scraped off the clinker-like, vitreous brick without leaving any very considerable residue.

4. The fourth class of brick colorations refers to those which are formed only after the manufacture of the brick, or after they are put into use, and in most cases are an evidence of destruction. These consist, for the largest part, of salt efflorescences which quietly carry on their work of destruction by repeatedly disappearing and recrystallizing, or of organic compounds which attain the same result in a longer time and with less energy. The main factor in both is moisture.

The destruction of brick by the formation of salts which come to the surface from the interior, is especially prominent with porous, soft-burned material, in whose manufacture sufficient heat was not applied to destroy the soluble salts or to convert their elements into insoluble compounds of silicic acid.

These efflorescences of salts, commonly called saltpeter,

consist in many cases of sodium bicarbonate, sulphates, especially of soda and magnesia, chlorine compounds, etc. Saltpeter is present only when the brick has come in contact with decaying organic matter.

To ascribe the appearance of the so-called saltpeter to the influence of low organisms, as is often done, seems unnecessary. With light-colored brick exclusively (and not on red or dark-colored brick), we observe an action of organisms which makes itself especially obnoxious by its intensely green or yellow color. This is due to microscopic plants, *algae*, which grow upon and draw their nourishment from the moist and porous surfaces of the brick, and whose dying generations cover the latter with a black, humus-like substance. It appears that the growth of these organisms is favored less by the composition of the material than by its color, for they are found not only upon the ordinary cream-colored bricks with a calcareous body, but also on fire-bricks, with great regularity, whenever the latter are exposed to moisture and are protected from the direct light of the sun. At the same time they are found only on the light-colored portion of the brick, but never in places where a dark coating has been formed. It seems a difficult task to find protection against this enemy which often makes its appearance only after the bricks, of perfect color, are walled up, and which are then not easily accessible for the destruction of the vegetation. The only means of destroying this enemy of light-colored brick seems to be the treatment with caustics, and Dr. Fruehling, at the last annual convention, has recommended as such the coating of walls covered with the green scum with a solution of calcium sulphite. Yet there might arise doubts as to whether it will protect for a long time since it is itself subject to a rapid change. It would perhaps be advisable to substitute a stable poison for organic growths, like zinc sulphate, but not zinc chloride, owing to the efflorescence to be expected from the latter salt, or arsenic.

## The Colors of Bricks

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When we examine the pure white or nearly white burning clays which serve as materials for the porcelain and stoneware industries, we will always find that they contain as essential ingredients alumina, silica and water, but other constituents only in very small quantities. These are materials which are produced by the weathering of feldspar and are usually still found at the places at which they were produced. But if these clays are carried away by water it will be unavoidable that they are mixed with other substances which are likewise produced by weathering and disintegration in other places and which impart to the clay mixture thus obtained a more or less intense color. The materials used in the brick industry are of this kind.

The number of substances which color the clay is quite limited so far as practical work is concerned. If we neglect the rare elements occurring in it only in extremely small quantities and which are hardly ever present in quantities larger than one-tenth of one per cent, like titanic acid, vanadic acid and similar constituents which do not influence the color, there are to be considered only the iron and manganese oxides, and also the calcium and magnesium carbonates, which give rise to the various colors of bricks. According to the different quantities of these constituents, the varying division of the same, the different temperatures to which the bricks are exposed, the difference of texture and especially of porosity, and finally the difference in the action of the fire-gases, the colors produced will vary within wide limits. One cannot say that two clays which have exactly the same percentage composition will give rise to the same color on burning, but the result in regard to color may be quite different, for example, owing to the different division of the iron oxide and the different texture of the brick ; it may be possible that for these reasons a clay high in iron will express the color of the iron oxide less intensely than one which contains less iron oxide.

I would like to remark at the beginning that the colors of the unburned clay stand in no relation to the color after burning, and hence are no guarantee for a definite appearance of color after the burn. The iron which is washed into the clays may have a very different color when in the form of iron silicates or ferric hydroxides or ferric oxide or ferrous compounds and may pass from yellow into gray or bluish green. Again, it is often accompanied by organic substances.

Beside the iron oxide there occurs only the manganese oxide which assists in producing color on burning. This is always associated with the iron oxides and usually in such a small ratio when compared with the quantity by weight of the iron that ordinarily it need not be considered. Also there are found in many clays not inconsiderable quantities of calcium and magnesium carbonates, which are pure white by themselves but which by their presence modify the color of the iron oxide.

The colors which clay wares assume are thus dependent upon various conditions which influence the color simultaneously, the one more, the other less.

The most important factors are :

First, the quantity of iron oxide contained in the clay.

Second, the other constituents of the clay accompanying the iron.

Third, the composition of the fire-gases during the burning.

Fourth, the degree of vitrification.

Fifth, the temperature at which they are burned.

Let us now consider these five factors.

i. The iron oxide in the pure condition is a red body. If it is exposed to only a low temperature, it possesses a yellowish red color when in the finest state of division. On being heated strongly it will always become denser and darker, and at a high heat it will assume a dark red bluish color. According to the method of preparation from different substances it will vary somewhat, even in this red color, and will sometimes tinge into

a brown and again into a blue. This color, however, will be stable only when the iron oxide is heated in an atmosphere containing an excess of oxygen. If the heating is done in the presence of reducing gases, carbon monoxide or hydrocarbons, it will be reduced to ferrous oxide or to intermediate stages between ferric and ferrous oxide, or to ferrous oxide and metallic iron and finally to metallic iron, assuming in all of these combinations a blackish color. But these bodies again take up, when heated in air containing oxygen, the quantity of oxygen lost, again giving rise to the formation of iron oxide and again representing the red color of the original iron oxide, but usually in a different shade. In general all coloring phenomena of clayware run along a similar course. The degree of color which they assume is as a rule dependent upon the quantity of iron oxide enclosed; the greater the content of iron the deeper will be the color which they assume.

2. The constituents which are white in themselves, alumina, lime and magnesia, exert a decided effect upon the color. If the content of iron oxide in a clay is small, and that of alumina large, and the burning temperature high, the clays will assume only a more or less yellow or yellowish brown color, which, with a smaller content of alumina and increasing content of iron, passes regularly through all the shades from yellowish brown to reddish brown. Only with a content of about 5 per cent of iron oxide does a decided red color appear which is intensified still more by a higher content of iron.

Similarly, as in the case of a high alumina content, the color of the clay is bleached also by a content of calcium carbonate, which frequently is associated with a small content of magnesium carbonate. As in the previous case, the color of the iron oxide is bleached the more, the higher the ware is heated. If the content of lime is about double the quantity of the iron oxide, the red color of the iron oxide disappears completely at a sufficiently high temperature, its place being taken by a yellowish green color.

It may thus be said in general that only those clays will possess a red color which have a large content of iron with a

moderate or low content of alumina and lime. If the content of alumina is increased with a simultaneous decrease of the iron oxide, more or less yellowish brown or yellow colors are obtained, but if the clay contains carbonates of the alkaline earths, the color is changed to a yellowish green. If, hence, it is intended to produce other shades of color than those which the clay possesses in itself, for instance, the change of color from red to yellow, it is only necessary to add a white burning clay, or one with but little color, whose content of alumina is to be as large as possible. The colors thus obtained will run through the shades of red, brown, yellowish brown, and yellow; another means might be an addition of calcareous material, chalk or lime marl. On changing a yellow burning clay to a red burning one, it will be necessary to add a very ferruginous material, as a clay high in iron, ochre, or bog iron ore. This addition would easily lead to the desired result in the case of clays free from lime, but in calcareous clays it will exert an effect which is the smaller as the content of lime increases. It is self-evident that additions of this sort also change the temperature necessary for burning. On adding light burning material high in alumina, as a rule the burning temperature is raised; on adding calcium carbonate or iron oxide, it must be lowered.

3. The composition of the fire-gases which are used in burning, is of the greatest importance in regards to the color of clay wares. It is a well-known fact that the kiln construction is of great influence in this respect, and those who operate different kiln systems will know that the colors vary in the same raw material according to whether the material is burned in this or that kiln. The differences which are thus produced are explained if one considers the behavior of the iron oxide under oxidizing or reducing conditions of firing. The sulphur content of the coal likewise plays an important rôle. As I have mentioned previously, the compounds of ferric iron are always changed to ferrous compounds by the action of reducing gases (carbon monoxide, hydrocarbons, hydrogen), or when the iron oxide is present in the clay in the free state, even to metallic iron. In this manner the clay assumes a gray color. If during

the burning a trial is drawn from the kiln, it will be found that this gray color, in the presence of much iron, will even become a black. On being exposed to an oxidizing atmosphere, if the body is still porous, the ferrous iron or metallic iron will again be changed very rapidly to the red or yellow iron oxide. The denser the body becomes, that is, the less access it affords to oxygen, the slower will the re-formation of iron oxide take place, and if the body is closed completely it will remain black or gray, or at the most will assume a brownish or reddish color only at the surface. In general we have in our kilns always a change of oxidizing and reducing effects, in the one system the change occurs ordinarily in larger, in the other in shorter intervals. In periodic kilns reduction occurs, as a rule, in the first period of the burn, becoming less frequent and weaker towards the end of the burn ; in continuous kilns, however, the conditions will always be the same. In all kilns, unless reduction is provided for during the cooling period, cooling will take place in an oxidizing atmosphere. For this reason the reducing effect is observed sometimes more and again less after cooling, giving rise to greenish or again to a grayish color, the first with calcareous, the second with yellow to red burning materials, free from lime.

The sulphur content of the coal which appears in the fire-gases in the form of sulphurous acid, plays an important rôle in the color phenomena. This is especially prominent in the case of calcareous clays on whose surface a formation of calcium sulphate takes place. If in consequence the lime cannot enter into the formation of the silicate, the coloring effect of the iron oxides will not be influenced by the lime, and sometimes a very intense red color will be produced in the places exposed to the fire. After a reduction the red spots will disappear, but since the conditions of vitrification have become different by the absorption of sulphuric acid, the color of the places which once have become spotted will differ in shade.

4. The degree of vitrification, which the clay undergoes in burning, is likewise of influence in regard to the color which it assumes. In porous materials containing many air pores, the colors will always be lighter, in denser materials always darker, with the same content of iron.

5. The burning temperature also gives rise to different colors in a similar manner. We have already seen that the coloring iron oxide always assumes a darker color with a continually rising temperature. This is also true for its compounds, and hence we observe that the clays which are burned at a higher temperature possess, in general, a dark color. However, the opposite is also true when the clay contains a small percentage of calcium carbonate whose quantity is not sufficient to remove entirely the red color due to the presence of the iron oxide. In this case the lime at a higher temperature still tends to destroy the color of the iron oxide, and hence on stronger burning a lighter color is produced. In all materials free from lime the properties of the iron oxide alone are the governing factors.

From what has been said only those color changes can be explained which the materials show at the fracture, and provided a change in the color, due to an extremely thin superficial layer, has not taken place; that is, in so far as the surface is free from depositions. As a rule these depositions are caused by salts, usually sulphates, which assume a white color on burning, or are partially vitrified together with the clay, and hence appear somewhat colored. The salts are found either naturally in the clay or in the water used for smoking, and on drying reach the exposed surfaces on which evaporation takes place and remain there as a fine crystalline coating. These deposits may also be due to the influence of the fire in the first stages of the burn. In this case they are produced by the condensation of water from the fire-gases upon the surfaces of the bricks. The gases, besides water, always contain constituents of the ash which are volatilized at a higher temperature, and also the sulphurous acid which is the product of combustion of an iron sulphide always present in coal, and finally particles of fine ashes. If now the water is condensed upon the ware it is clear that these substances are also deposited upon it, and these exert a considerable influence on the color. Whether these coatings have already been produced before burning, or whether they owe their origin to the fire-gases during the first stage of the burn, may be decided by

inspection. In the first case those surfaces of the ware which were covered on drying are free from the coating, but in the latter those which were covered in the setting of the ware. Since these surfaces are not always the same it is very easy to draw a conclusion in regard to the time during which the coatings were produced. On burning, the salt-like incrustations, as a rule, vitrify to the surface so intimately that they cannot be removed from it, and usually they have been decomposed by vitrification and rendered insoluble, thus giving the ware a permanent surface color.

The brick may again be colored after being walled up. This color originates from the salts which have remained undecomposed in the pores of the brick and now come to the surface on being moistened with water, causing efflorescence. These may be sulphates which were already present in the clay, or which have been formed only in burning through the action of sulphurous acid from the coal and had not been removed by reducing conditions. In this case the efflorescence is white and may be avoided by reducing conditions of the fire-gases brought about in the last stage of the burn. But greenish or yellowish green compounds may be due to vanadic acid which is always found present, but only in small quantities. These can likewise be removed by the reducing action of the fire-gases, the vanadic acid being thus reduced and fixed in the clay as oxide of vanadium.

The colors which a greater or smaller content of iron oxide will produce in the clay, may be determined by a number of mixtures of different clays with a known content of iron oxide. The trials made for this purpose were mixed at the factory of Mr. March according to definite proportions, two clays always being mixed in such proportion that for 0.1, 0.2, 0.3, etc., of the one there was added one part by weight of the other and, similarly, with the second clay. For the mixtures of clay five clays were used: the clay highest in iron, from Helmstedt, contains 21.3 per cent of iron oxide in the ignited condition; the Rathenow clay 8.02 per cent; the clay from Belgern, burning to a yellow color, 4.63 per cent; the clay from Tschirn 1.02 per cent; and the Loethain clay 0.8 per cent. On comparing the

colors which the clays assume with their different contents of iron oxide it will be observed that the latter does not increase in coloring power above a certain percentage, while a decrease gives rise to marked differences in color. Those trials in which the content of iron oxide lies between 21.3 and 8.5 per cent do not differ essentially in color; considerable fluctuations appear only with a low content of the ferric oxide; the mixtures become lighter, and finally turn to white completely. The color of the Belgern clay, whose content of iron oxide rises as high as 4.6 per cent, is characteristic, its color being an intense yellow. On the other hand, a mixture of the Loethain and the Helmstedt clay with a content of iron oxide of 4.2 per cent is of quite a pale red color. Without doubt the iron oxide plays a rôle in all these coloring phenomena in proportion to its quantity, but this is not the only consideration which is to be observed. The chemical constitution of the clay, the mechanical division of the coloring ingredient, the iron oxide, the intensity of burning, and finally the manner in which the fire-gases have acted upon the trials during the burning; all these factors are of importance in regard to the shade of color produced.

The mixtures were carried out in the following proportions:

## I

## CLAY FROM HELMSTEDT AND CLAY FROM LOETHAIN

(Iron oxide, 21.3 per cent)

(Iron oxide, 0.8 per cent)

	Color.	Content of iron oxide. Per cent.
Pure Helmstedt clay		21.3
10 parts Helmstedt, 4 parts Loethain clay	dark red,	15.4
10 parts Helmstedt, 8 parts Loethain clay	not differing	12.2
10 parts Helmstedt, 10 parts Loethain clay	much	11.0
8 parts Helmstedt, 10 parts Loethain clay	red	9.9
6 parts Helmstedt, 10 parts Loethain clay	brighter red	8.5
5 parts Helmstedt, 10 parts Loethain clay	still brighter red	7.6
4 parts Helmstedt, 10 parts Loethain clay	bright red	6.6
3 parts Helmstedt, 10 parts Loethain clay	yellow	5.5
2 parts Helmstedt, 10 parts Loethain clay	light yellow	4.2
1 part Helmstedt, 10 parts Loethain clay	white-yellow	2.7
½ part Helmstedt, 10 parts Loethain clay	nearly white	1.8
¼ part Helmstedt, 10 parts Loethain clay	white	1.3
Pure Loethain clay		0.8

## II

## CLAY FROM RATHENOW (WASHED) AND CLAY FROM BELGERN

(Iron oxide, 8 per cent)

(Iron oxide, 4.6 per cent)

	Color.	Content of iron oxide. Per cent.
Pure Rathenow clay	dark red	8.0
10 parts Rathenow, 1 part Belgern clay		7.7
10 parts Rathenow, 2 parts Belgern clay		7.4
10 parts Rathenow, 4 parts Belgern clay		7.0
10 parts Rathenow, 6 parts Belgern clay		6.7
10 parts Rathenow, 8 parts Belgern clay	the colors decrease	6.5 6.3
10 parts Rathenow, 10 parts Belgern clay	uniformly in intensity	6.1 5.9
8 parts Rathenow, 10 parts Belgern clay		5.6
6 parts Rathenow, 10 parts Belgern clay		5.2
4 parts Rathenow, 10 parts Belgern clay		4.9
2 parts Rathenow, 10 parts Belgern clay		4.8
1 part Rathenow, 10 parts Belgern clay		4.6
½ part Rathenow, 10 parts Belgern clay		
Pure clay from Belgern	yellow	

On burning harder, the colors become somewhat darker but decrease uniformly in intensity.

## III

## CLAY FROM HELMSTEDT AND CLAY FROM TSCHIRN

(Iron oxide, 23.1 per cent)

(Iron oxide, 1 per cent)

	Color.	Content of iron oxide. Per cent.
10 parts Helmstedt, 4 parts Tschirn clay	dark red	15.5
10 parts Helmstedt, 8 parts Tschirn clay	dark red	12.3
8 parts Helmstedt, 10 parts Tschirn clay	dark red	10.0
6 parts Helmstedt, 10 parts Tschirn clay	dark red	8.6
½ part Helmstedt, 10 parts Tschirn clay	light yellow	2.0
¼ part Helmstedt, 10 parts Tschirn clay	lighter yellow	1.5
Pure clay from Tschirn	nearly white	1.0

The trials omitted between the fourth and fifth line give rise to changing colors, and hence are not tabulated.

## IV

Clay from Belgern and Clay from Loethain  
(Iron oxide, 4.6 per cent)      (Iron oxide, 0.8 per cent)

	Color.	Content of iron oxide. Per cent.
Pure clay from Belgern	yellow	4.6
10 parts Belgern, 2 parts Loethain clay	lighter yellow	4.0
10 parts Belgern, 6 parts Loethain clay	yellow	3.2
10 parts Belgern, 8 parts Loethain clay		2.9
10 parts Belgern, 10 parts Loethain clay		2.7
8 parts Belgern, 10 parts Loethain clay	gradually changing	2.5
6 parts Belgern, 10 parts Loethain clay		2.2
4 parts Belgern, 10 parts Loethain clay	to white	1.9
2 parts Belgern, 10 parts Loethain clay		1.4
1 part Belgern, 10 parts Loethain clay		1.1
Pure clay from Loethain		0.8

### The Influence of the Sulphur in Coal upon Clay Wares

W. H. ZIMMER, PH.D., TRANSLATOR

When examining our old brick buildings of northern Germany the question is often asked, why have these resisted the attacks of the northern climate so well, while now it is difficult to make brick of the same resisting power? On examining the old brick more closely, the reasons for their greater resisting power will hardly become evident from their appearance. They are made as a rule in a larger size, hence offering greater difficulty in burning uniformly throughout. The fracture does not indicate a better mixture of the body than is now possible with the better mechanical appliances on hand; on the contrary they are usually less homogeneous. The glazes applied on them are simple, easily fusible, lead glazes which frequently show but little wear. When, however, we study our present front brick, we

find that many will certainly show the same or a greater durability than the old brick; but some, after a short time, indicate such distinct signs of destruction, due to the influence of the atmosphere, that they do not promise a long resistance to the destructive action of the weather.

It may be assumed that in olden times as well as now brick materials were often used which are not weather-resisting, but that only the better kind has come down for our inspection since, in the course of centuries, the less resistant materials have been destroyed. Be it as it may, the view is widely extant among architects as well as brickmakers that the brick material of old has been more resistant to weather than the average of the brick manufactured to-day.

It was endeavored to explain this greater resistance of the old building material by a better and more energetic treatment of the raw material and its better selection. It has been said that the old brickmakers not only selected the clays in regard to their suitability to the manufacture of brick more carefully, but that they dug it long before using, allowing it to freeze thoroughly, spading it over many times, thus subjecting it to the bleaching of the rains and the weathering action of the air. This may be very true and may be found based on the customs of the old brickmakers, but it cannot be denied (and this is proved by the old bricks themselves) that with the means existing to-day the structure of the raw materials is destroyed much more thoroughly than was customary in the olden times. At any rate the cause of the greater resistance of the older brick materials cannot be founded on the presumed better working of the clay. We believe that the cause of the deterioration in the weather resistance of the brick is to be sought in the fact that the burning must now take place almost exclusively with the use of fossil fuel, peat being used in the smallest measure, lignite in the greater and coal in the greatest, while formerly wood alone served as fuel in burning.

It is a fact not to be disputed that for the manufacture of all clay wares of whatever kind, wood is the most suitable and safest but also the most expensive fuel, and that for the last reason,

with the exception of a few cases, the much cheaper coal is preferred. If we now compare the composition of the wood with that of the coal the reasons for its greater suitability may be easily seen. Wood, chemically considered, is a combination of carbon, hydrogen, and oxygen, which are associated only with very small quantities of inorganic matter, ash. The latter consists principally of potassium carbonate. The hydrogen and oxygen are approximately in the proportion in which they unite to form water; hence the active constituent of the fuel is essentially the carbon. In the fossil fuels produced by the decay of vegetable residue, however, there are found, beside the organic constituents (carbon, hydrogen, oxygen), considerable quantities of inorganic substances. In some fuels these amount to 30 and 40 per cent. They become especially injurious by being converted into dust in the kiln which cannot be avoided and also by the volatilization of some of the constituents and absorption of these by the clay. The sulphur compounds of the clay which often are present in considerable quantity are especially injurious in this respect since they likewise are transferred to the fire-gases. The sulphur as a rule is found in the fuel in the form of iron sulphide, in brass-yellow, cup-like deposits, grown in the cleavage veins of the coal or finely divided and invisible. In the latter form, iron sulphide especially occurs in the lignite and peat.

On the combustion of coal the iron sulphide, under the action of the heat and the oxygen of the atmospheric air, is changed to iron oxide, the sulphur, however, being transformed to sulphurous acid which mingles with the fire-gases. This gas may always be noticed in the fire-gases originating from fossil fuels by its smell. This sulphurous acid is partially, sometimes even completely, taken up by the clay. If oxygen is still present in the fire-gases the sulphurous acid is oxidized to sulphuric acid under the influence of some basic body contained in the clay, like potash, soda, lime, magnesia and as such it is taken up by the bricks. This becomes especially pronounced in the case of bricks which contain calcium carbonate and magnesium carbonate so that they may be completely changed in color by the absorption of sulphuric acid, which on the surface may be

present in quantities up to 10 per cent and over. Under the influence of carbon monoxide and the hydrocarbons from the fuel which are produced when oxygen is lacking in the fire-gases, the sulphuric acid taken up by the brick is again liberated in the form of sulphurous acid and under the influence of these may pass out of the kiln. But periodically when the coal has burned down, and burning takes place with a smokeless flame, sulphurous acid is again taken to the brick from the fuel to form sulphates. Such an absorption of sulphuric acid compounds by the brick will take place more readily the easier oxidizing conditions are produced in the kiln construction used. The continuous kiln system, so generally used of late, always burns with an excess of air unless special arrangements are made to burn with a smoky flame. In the old systems a wider fluctuation in the composition of the fire-gases takes place, the burning being smoky at one time and then again clear and free from smoke. The introduction of sulphuric acid salts into the brick material is always more to be feared in the use of fossil fuel than in the use of wood for burning brick. Although in the latter case the presence of such salts in the raw clay is not excluded, the salts present in the clay, however, are destroyed more easily and safely in the burning with wood than in the burning with coal. For this reason we must always assume the presence of the injurious salts in a greater measure in the brick of modern manufacture than in the old brick.

Let us see how the presence of sulphates in a brick may injure their weather-resisting power. We cannot assume a chemical action of the salts upon the substance of the brick, but we may detect a mechanical effect since they are more or less soluble in water, an action quite similar to that which ice exerts upon brick. As the ice on crystallization brings about the destruction of the brick structure, so we may also assume this in the case of the soluble salts since these on the evaporation of water again crystallize from solution. At the same time the salts are not deposited as an extremely fine powder upon the surface of the brick, but corresponding to the distribution of the solution in the pores of the brick the smallest parti-

cles migrate from place to place; they always group together to form separate crystals of larger or smaller dimensions and thus exert a pressure upon the neighboring particles. The destruction of the bricks will take place most easily where the salts tend to form large crystals. This is especially true of sodium sulphate and magnesium sulphate, but to a less degree of potassium and calcium sulphates. The same action is renewed after every wetting of the bricks and subsequent drying; though frequently the single effect, on account of the small quantity of the salts dissolved, is slight, still the total effect on account of the frequent repetition of the same action becomes great. If the quantity of the salts present in the brick is large they will appear on the surface; it is said that the bricks are 'salt petered' because formerly the formation of salt peter in the same was always assumed, which, however, occurs only in the presence of organic bodies. In most cases the salts are compounds of sulphuric acid with potash, soda, lime or magnesia, whose bases are always derived from the material of the brick, but whose content of sulphuric acid usually originated from the coal with which the bricks are burned. The destruction of the brick in the presence of large quantities of these salts is naturally very rapid, and the more so the more they are exposed to a change in the degree of moisture and the softer they are burned, that is, the looser their substance has remained. In the presence of smaller quantities, when the salts can not find room in the pores of the brick, but appear on the surface of the same, a gradual decomposition of the brick takes place; ordinarily such bricks resist the influence of the weather for a number of years, and only then the destructive influence gradually makes its appearance.

But the burning with coal has a great influence, not only upon the weather-resisting power of the brick (in the case of coal which contains more or less sulphur, from the minimum quantities up to 4 per cent of iron sulphide), but it also exerts a great influence upon the color of the brick surfaces. The color assumed by the brick on burning may often be traced back to its content of sulphuric acid. This is especially striking with

those brick clays which contain finely divided calcium carbonate. Such clays, if their content of lime is large as compared with the content of ferric oxide, do not assume the color ordinarily given by this oxide to the clay (yellowish brown, reddish brown or red), but they show a lighter color (flesh color or yellowish gray). This color is to be referred to the presence of a silicate consisting of iron oxide, alumina, lime, and silica.

If thus the lime is united with an acid, which is not expelled by silica at the highest temperature of the kiln, the formation of such silicates cannot take place since the lime must remain outside of this combination. In this case only the iron oxide, alumina and silica unite, the color of this compound being much darker, usually red. The absorption of sulphuric acid from the fire-gases prevents the lime from entering into combination with the silicate of the brick, since the calcium sulphate is not decomposed by the silicic acid or its compounds in a kiln atmosphere containing oxygen. Hence the bricks are often of a red superficial color, while at the fracture and places not exposed they have ordinarily assumed the normal yellow color. In this case the periodic presence of smoky fire-gases again gives rise to a decomposition of the sulphates produced, the sulphuric acid being changed to sulphurous acid, which in this state may be easily expelled. The color which now becomes yellow will, however, assume a different shade in such places which had once been red during the burn owing to the different degree of vitrification; hence, such places are made somewhat prominent, especially when the decomposition of the sulphates takes place only at so high a temperature that the vitrification of the brick is quite pronounced. In firing with wood such a discoloration of the material is not to be feared, owing to the lack of sulphur, but it will appear on firing with peat, lignite, or coal in a greater degree the higher the content of sulphur in the fuel, and the less the kiln construction is suited for filling the kiln space with a smoky atmosphere from time to time. Experience has taught us that it is much more difficult to produce pure yellow-colored brick with the later continuous kiln systems than with the older more wasteful kilns which are often retained for this purpose.

The absorption of sulphuric acid from the fire-gases also becomes noticeable in regard to color in clays other than those containing lime and burning yellow, although not to such a marked extent as in the case of the former; the places at which the absorption took place may always be recognized after the sulphuric acid has been expelled by smoky fire-gases, by the different degree of vitrification occurring in these places, differing from the other portions by a shade or two in color.

In the use of glazes on face-brick and terra cotta which are exposed to the weather in the walls of buildings, the absorption of the sulphuric acid compounds by the body, plays an important part. That glazed bricks are more easily destroyed by frost than the same unglazed brick is an experience that is met with very often. This is founded on the fact that the glaze prevents the expulsion of the ice crystals from the pores of the surface, which finally crack off the entire glazed surface. But the penetration of water into the brick, though made more difficult by the layer of glaze, is by no means prevented. Water will always have an opportunity to penetrate behind the layer of glaze, through defects which are always present in the coating of glaze and through the joints between the bricks. The crystallization of the ice exerts an action analogous to the crystallization of the sulphates, present in the clay, on the addition of moisture and drying out of the same. A splitting off of the glaze layer owing to crystallization takes place and the action of the ice is continued by the salts in the interior of the brick in summer. That the glazes on the old brick may have been more durable owing to a different composition, cannot well be assumed. There is always used for this purpose a mixture of lead oxide, clay and sand, though to-day a more uniform composition may be obtained by weighing the constituents, while formerly it was customary to measure by volume. As a whole, the glazes must have had the same composition in olden times as they have now, for more resistant glazes, higher in silica and alumina, could not have been melted upon easily fusible bodies, any easier than we can to-day.

Let us now examine the method according to which the

glazed bricks are manufactured at the present time. The bricks are first burned; this, of course, is accomplished with coal containing sulphur, as a fuel. The burned bricks are then shaded according to the color desired for face-brick. The soft-burned and discolored bricks thus set aside, are good enough to be coated with a colored glaze and reburned because slight defects of the surface are not objectionable. These bricks, of course, have the tendency to be destroyed by weathering, owing to the deposition of salts due to the sulphur present in the fire-gases. The burning of the glaze is frequently accomplished with wood, avoiding smoke as much as possible during fusion; that is, under conditions in which the salts of the body are not destroyed. Still people are surprised when, after a few years, the glaze coating of the brick splits off. If the bricks were first burned with wood, this would not take place, for then such irregularities in color would not appear, and hence there would be no necessity of excluding some bricks for the purpose of glazing. It is also quite likely that formerly (as it is still being practiced where wood is used as fuel) the brick were not burned twice, but were glazed in the green condition, the glazed bricks being burned in the same kiln with the unglazed bricks. In this manner the danger that the body of the glazed bricks might take up salts is decreased still more. It appears very likely that this greater resistance of the glazed bricks is to be ascribed only to this procedure, and it should be the endeavor of every one, even to-day, to pay some attention to these conditions.

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#### A Contribution to the Knowledge of Efflorescence on Terra Cotta

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W. H. ZIMMER, PH.D., TRANSLATOR

Among all those phenomena giving rise to imperfect products, which make the manufacture of uniformly colored face-brick and terra cotta more difficult, the most troublesome are the

salt-like efflorescences so hard to remove even when present in very small quantities. They are found chiefly in places promoting rapid evaporation ; that is, on corners and edges, and the prominent parts of molded or modeled objects, their formation being confined chiefly to the drying process. They make the manufacture all the more difficult and uncertain since they frequently cannot be detected by the unaided eye before burning, and become visible only afterward, especially in clays which are light-colored in the raw condition.

The efflorescences, which apparently are the more prominent the slower the drying process is carried on, have so far not been deemed of sufficient importance and have not been made the subject of close study. Our text-books on brick manufacture contain nothing concerning them. They deserve much attention, since they are usually found less on the sandy, and for this reason rough and porous, materials of coarse brick than on the finer, denser, and smoother materials of the better and more valuable products of the brick industry.

The neglect of these efflorescences, owing to the difficulty of observing them, has gone so far that a number of establishments were under the belief that the cause of their failures in regard to the production of good colors was due to the burning, the defects not being removed in spite of experiments continued for years, while as a matter of fact the trouble in most cases is to be traced back to the drying process.

Not only the water which is used for the softening of the clay contains, without exception, a larger or smaller quantity of mineral constituents in solution, but also the clay has the property to retain substances soluble in water, which are formed by the never-ending decomposition in the deposit; and the more plastic a clay is, the more will it retain. If the clay has been exposed to weathering during the winter, which is always necessary for the better products, a new opportunity is afforded for the often energetic formation of soluble salts, especially when finely divided iron sulphide is present. A leaching and removal of these salts will hardly take place to any appreciable extent by the atmospheric precipitates (though this is commonly assumed)

for several reasons. First, because the moistening of clay makes it impenetrable, preventing leaching of any kind, and again because the process of formation of the salts is concluded only after many years. This formation is especially facilitated by the weathering of clay by frost and hence begins to be most energetic when the clay has been brought to the condition suitable for manufacture. The removal of soluble salts formed by the weathering of the clay during the winter by rain or snow can hence be only a very superficial one, and other industries have shown the impossibility of removing, even approximately, soluble compounds from substances possessing physical properties similar to clays, on a large scale. The effect of soluble salts becomes the more unpleasant, since the process of formation goes on during the working of the clay and during the drying, and since such saline clays have a special tendency to give rise in the kiln during the water-smoking process to other discoloring, salt-like efflorescences.

Since the evaporation of the water on drying can take place only at the surface or only to a slight depth in the case of sandy, porous clays, all the moisture must first be taken to the surface by capillary attraction, before it can be evaporated. In this manner the salts taken into solution are brought to the surface where they remain. The denser the solution of salts, the closer to the surface will they be deposited.

The salts, thus segregated after the removal of the water, form either a dusty coating or wart-like crystals of microscopic size, very difficult to observe by the inexperienced eye if their color is similar to that of the clay, because they enclose a clayey substance within their aggregations. They become decidedly visible only after burning, being usually white, gray, or yellowish, and are then firmly burned into the clay body, being difficult to remove either mechanically or chemically.

The removal of these undesirable coatings has often been the subject of empirical experiments but only in a few cases have these been entirely successful. The means of removing them are either mechanical (rubbing off, brushing, dipping in tar or similar substance) or chemical. The former can be used

only for some products and for discolorations which do not adhere very firmly; the latter presume an exact knowledge of the chemical composition. Owing to the slight consideration given to the soluble salts contained in the clay on account of their small amounts in practice as well as in the scientific examinations of clays, the chemical composition of this part of the clay is hardly ever given the proper attention and still it is of importance because only knowledge of the kind and quantity will show the means of converting them into insoluble, and hence harmless, compounds.

In many cases such efflorescence is considered as originating from calcium sulphate, magnesium sulphate, calcium carbonate, and magnesium carbonate. Qualitative analysis has always shown me these, beside other constituents. We find, however, from the analyses quoted later on that the composition may differ very much in places close together; hence, the reagents for removing them must also be very different.

Among the different veins of clay used at the Siegersdorf works for the manufacture of face-brick and terra cotta, there have been observed two layers, one of an ash-gray, and another of a blackish clay which possesses the above bad quality, and hence in the manufacture of better products are to be kept separated from the other materials of the bank which do not contain the salts. These clays in the raw condition show a distinct salt-like efflorescence on the corners and edges of the lumps on being exposed to the air for some time. In order to determine the nature of this efflorescence, a larger quantity of the clay was boiled with distilled water and, after settling, the perfectly clear liquid was evaporated to dryness and the salt obtained was analyzed. The salt obtained from the gray clay, *A*, was crystalline, colored dark by organic matter, and slightly deliquescent; that obtained from the blackish clay, *B*, was yellowish green, extremely hygroscopic, deliquescing in a short time to a sirup-like fluid in moist air.

The composition of these salts was found to be :

	From gray clay. <i>A</i> Per cent.	From black clay. <i>B</i> Per cent.
Sulphuric acid - - -	55.13	55.05
Lime - - -	11.24	trace
Magnesia - - -	11.10	4.42
Ferric oxide with small quantities of ferrous oxide - - -	6.22	32.15
Alumina - - -	0.41	2.16
Alkalies - - -	4.82	1.28
Organic matter - - -	5.41	trace
Water, chlorine, and constituents not determined - - -	5.67	4.94
	<hr/> 100.00	<hr/> 100.00

From this the composition is calculated as follows:

	<i>A</i> Per cent.	<i>B</i> Per cent.
Calcium sulphate - - -	27.84	trace
Magnesium sulphate - - -	33.30	13.26
Sulphate of iron - - -	15.55	72.20
Aluminum sulphate - - -	1.39	7.25
Alkaline sulphates - - -	8.82	2.32
Organic matter - - -	5.41	trace
Water and constituents not determined	5.67	4.94
	<hr/> 100.00	<hr/> 100.00

It is thus seen that in *A* the salts of calcium, magnesium and the alkalies predominate, and all possess a decided tendency to crystallize, this being the cause of efflorescence, and hence may exert a very injurious influence even in smaller quantities. In *B* the deliquescent salts of iron and alumina predominate, which crystallize with difficulty and disturb the crystallization of other salts, thus being less injurious even in larger amounts than the first.

That the soluble salts contained in the bricks are really concentrated on the surface by drying, is proved analytically in the examination of an ordinary brick made from these materials

which on its surface showed gray, wart-like crystalline segregations when in the air-dry state. The outside layer, about 0.5 mm. thick, has a sulphuric acid content of 1.51 per cent, the interior only of 0.70 per cent. Assuming the content of sulphuric acid in the soluble salts as being 55 per cent according to the above analysis, this would correspond to a content of soluble matter, giving rise to efflorescence, of 2.75 per cent in the outside layer, 0.5 mm. thick, and of 1.27 per cent in the interior of the brick.

At the last annual convention of the society, the question of preventing the efflorescence mentioned was discussed in a paper by Mr. Mertin. Owing to the importance of the subject, which has become the all-important question for many establishments, I believed that I should not hold back this communication, little as it is able to throw full light upon the phenomena of efflorescence. It will show this much, however, that the chemical removal of efflorescence by empirical trial, which is adapted to one condition, will be far from insuring a similar success at another place, and that the cost of the process will always be influenced by the quantity as well as the kind of the additions required for the fixing of the injurious salts.

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### Yellow and Green Efflorescence on Brick Fronts

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W. H. ZIMMER, PH.D., TRANSLATOR

Although the buff-burning, so-called lignite, clays are especially suited for the manufacture of front brick and terra cotta on account of the agreeable shades of color which they assume, the products manufactured from them often take on an undesirable coating, when exposed to atmospheric precipitations, with a yellow, intensely green, or even bluish green efflorescence, which, disagreeable in itself, after some time takes on a dirty, brown, or blackish color. The phenomenon appears to take place

most readily when the burning of the clay is not hard enough, and as a rule, not all of the products of the same burn are affected in this way, frequently only a few bricks. It often appears a few days after the ware has been taken from the kiln, sometimes after a longer while, especially after being exposed to the weather during the winter, and often after the products have been walled up. The last is the worst thing that could happen. The phenomenon is almost a general one, since it embraces all those clay ware manufacturers who obtain their materials from the great North German lignite horizon, which extends from the Oder to the Elbe, and farther, including the Lausitz, and a part of the province of Saxony. There are but few manufacturers who can boast of being entirely free from the evil and who have not experienced at least a periodic siege of the trouble.

A great deal of investigation has been carried on with reference to this disagreeable phenomenon, but the question as to its causes, which alone makes its prevention possible with safety, has not been solved in a satisfactory and conclusive manner. It has often been explained as being a growth of low organisms, an *algae*, which takes from the brick its mineral nourishment, and frequently this is really the cause.

In many cases, however, the colored efflorescence appearing on the surface of the clay has a salt-like character, and forms crystalline or wart-like deposits which permit only a mineral origin. Such efflorescences have been frequently examined and communications in regard to them are contained in the technical journals.

Efflorescences of this sort have often been considered as being colored metallic salts; thus Dr. Cohn<sup>1</sup> believes that they are iron salts which have not been decomposed on burning, and that others are suspected cobalt compounds; and I myself have succeeded in one case<sup>2</sup> in proving the pigment on a red brick with green efflorescence to be chromium compounds.

If in the investigation communicated to-day I ascribe the

<sup>1</sup> Thonindustrie Zeitung, No. 26, 1877.

<sup>2</sup> Deutsche Toepfer und Ziegler Zeitung, No. 34, 1877.

color to still another metal, I do not mean to imply that its presence in clay is in all cases the cause of the trouble, but often this will be true; hence the presence of the metal demands the attention of those who are in position to contribute to the explanation of the undesirable colorations.

In the case under investigation the material consisted of cream-colored face-brick, made from lignite clay near Wittenberg. These showed a very intense gold-yellow coating, recognized under the magnifying glass as wart-like accumulations of salts, spreading sometimes over entire surfaces, sometimes only over corners and edges, after they had been exposed to the weather for some time. Brick coated with a similarly colored efflorescence may be found on many brick buildings and all brick tiles. The colors remind one of the yellow colors of the chromates, and the green, of the chromium oxide, indicating the presence of a chromium compound, which I had proved in another case some time before. This appeared probable, since a small piece of brick, on being placed in cold water, colored the latter an intense yellow color, while the yellow color of the specimen disappeared entirely and the green partially. Undoubtedly one had to deal with a colored soluble salt. The yellow color, however, did not prove to be, as was assumed at first, due to chromic acid, but to vanadic acid.

Vanadium belongs to the rare, and for this reason less known, metals whose compounds possess very intense and lively, but also quite variable, colors, since many of its combinations are unstable. The compounds of the highest oxide of vanadium, vanadic acid, possess partly a very rich yellow color, but sometimes they are colorless. Under reducing influences, like organic matter or hydrogen sulphide, they are easily changed to the usually green or blue hydrous, or brown anhydrous, compounds of the lower degree of oxidation. For the purpose of proving this interesting body, the colored parts of a number of front brick were split off with a steel chisel and digested in cold distilled water. The gold-yellow, intensely colored solution, after having allowed the brick dust to settle, was evaporated to dryness, and on being heated for some time, lost

its yellow color almost entirely, but it again appeared on concentration. When strongly concentrated the solution assumed an intensely grass-green color, and after having been evaporated to dryness completely, a bluish green deliquescent salt was left behind, which redissolved in water and dilute nitric acid. From this salt, in which vanadium was proved beyond doubt, pure vanadic acid was prepared according to the method given by Rose.<sup>1</sup> The salt was dissolved in nitric acid and precipitated from the green solution of vanadium compounds with barium chloride and ammonia as a chocolate-colored powder, which, after washing and drying, was dissolved in hot concentrated sulphuric acid and poured into a large volume of cold water in order to precipitate the barium sulphate. The solution of vanadic and vanadous acid in sulphuric acid was of the color of copper sulphate; from this, by evaporating to dryness and driving off the sulphuric acid on subsequent oxidation with nitric acid, the vanadic acid was obtained as a red fused mass which showed all the characteristic reactions of vanadic acid. This is not the place to go into details, but those who are interested are referred to Rose's "Handbook of Analytical Chemistry."

It has long been known that vanadium not only accompanies many iron ores, though in extremely small quantities, but also many clays, yet it has not been observed that it exists as soluble compounds in burned clay. On account of the small amounts in which it exists it is never found in the ordinary course of analysis; but since the compounds possess such an extraordinary coloring power they may give rise to very conspicuous coloring phenomena.

Since in one and the same burn not all the products, but only a few pieces, show the colored efflorescence mentioned, it is to be assumed that the manner of burning (*i. e.*, the nature of the fire-gases) exerts an essential influence, inasmuch as the vanadium compound present may exist in the burned clay sometimes in the soluble and again in the insoluble form. What influences may effect these conditions must be left for further investigations.

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<sup>1</sup> "Handbook of Analytical Chemistry," 1871.

## On Vanadium Compounds in Lignite Clay and the Yellow and Green Discolorations Caused by Them on Terra Cotta

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W. H. ZIMMER, PH.D., TRANSLATOR

In the preceding article upon the examination of the disagreeable yellow and green efflorescence which very frequently is found on terra cotta manufactured from the lignite clays of northern Germany, and which appear after burning, or after walling up, I have shown that they consist of vanadium compounds. These can be dissolved out as soluble salts, after the burning of the clay and appear on the surface as wart-like crystalline segregations after the wetted products have again become dry, thus spoiling the appearance of the ware. Owing to the wide extent of this trouble we must give our attention to a substance which so far has not been considered, but which has proved to be an enemy to the clay industry, for only after knowing the causes of the evil are we enabled to look for means of remedying it.

It was first necessary, after proving qualitatively the presence of the colored vanadium compounds, to determine in what form and in what quantities these are present in the clay after burning, and again by what substances they are accompanied, in order to arrive at a starting-point as to the ways of removing the evil. For this purpose more extensive experiments were made.

First it was necessary to obtain sufficiently large quantities of the interesting green substance for the purpose of examination. As a material for the investigation face-bricks were used from the stock of a clay works on the Elbe, which were afflicted with the trouble, and which were placed at my disposal by the proprietor.

The material, in pieces of a maximum thickness of 1 cm., was placed in distilled water, the latter being poured off after a digestion of twenty-four hours, and being renewed as often (six times) as it showed a perceptible yellow color in the time

given. The gold-yellow liquid was evaporated to dryness, after settling out the brick dust, in a large platinum dish. On strong concentration and cooling, small orange-red crystals were formed from the yellowish green fluid; on evaporation there resulted a brownish yellow salt, green after rubbing to a powder. In this manner from 1550 grams of brick dust, 2.3995 grams of the salt containing vanadium could be obtained, corresponding to 0.155 per cent.

The composition of this salt which must be identical with the yellow or green substance found on brick fronts was, according to chemical analysis,

	Per cent.
Potash	19.82
Soda	3.17
Lime	3.24
Magnesia	3.34
Alumina and ferric oxide	0.77
Vanadic acid <sup>x</sup>	29.43
Molybdic acid	1.12
Sulphuric acid	15.70
Silicic acid	2.07
Chlorine	2.63
Water	18.25
Insoluble residue	<u>0.46</u>
	100.00

Distributing the acids among the bases the mixture of salts may be calculated to consist of:

	Per cent.
Potassium vanadate	44.38
Potassium sulphate	9.01
Calcium sulphate	7.97
Magnesium sulphate	10.02
Sodium molybdate	1.62
Sodium chloride	4.47
Soluble silicates	3.82
Water	18.25
Insoluble matter	<u>0.46</u>
	100.00

<sup>x</sup> Mean of two nearly coinciding weighings. The vanadic acid is obtained by precipitating ammonium vanadate after removing the alkaline earths and alumina with sodium carbonate and ammonium chloride and precipitating from the acid filtrate the molybdenum by means of hydrogen sulphide as molybdenum sulphide.

It is thus seen that the efflorescence consists essentially of potassium vanadate which is accompanied by calcium sulphate, magnesium sulphate, alkaline sulphates and salt, substances which form the salt-like efflorescence on walls.

The presence of molybdic acid, though only in small quantity, is interesting, it being a compound of the likewise rare metal, molybdenum, which in its properties is closely related to vanadium, and, like the latter, possesses intensely colored compounds.

Vanadium is a gray, difficultly fusing metal, and enters with oxygen into three combinations which may be contained in the clay.

The vanadous oxide (68.55 parts by weight of vanadium plus 8 parts by weight of oxygen) is black and produces no soluble compounds.

Vanadium oxide (68.55 vanadium plus 16 oxygen) whose soluble salts are usually green or blue.

Vanadic acid (68.55 vanadium plus 24 oxygen) all of whose salts are soluble and possess an intensely yellow color.

The coloring power of the vanadic salts is so extraordinarily intense that it becomes evident when all means of determining vanadic acid fail.

Beside the compounds mentioned there are some of the two last ones, that is, vanadates of vanadium oxide which possess an intensely green color, and in part are soluble in water, and also of great coloring power. These are produced from compounds of vanadic acid when they come in contact with reducing substances (dust, organic matter, hydrogen sulphide, etc.).

The compounds of the molybdenum oxide, corresponding to the vanadium oxide in their composition, are blue or purple; those of molybdic acid are colorless; vanadium molybdate, as well as molybdenum vanadate, is likewise green in color.

We are unquestionably dealing with these substances in the color phenomena under discussion, and the experience of practical work agrees perfectly with the theoretical facts. The yellow salts appearing at first are changed to green or blue compounds by the dust and impurities of water, by the soot which is

<sup>1</sup> Prof. Seger makes use of the old assumptions made by Berzelius, which are incorrect. This does not, however, affect Prof. Seger's results.—Ed.

deposited, or by the gases produced by decay. The colors are so characteristic that any one who has ever seen them on one material will immediately recognize them again. They are seen on nearly all building fronts, storage piles and brick plants which use lignite clay; and no establishment is known to use it which does not suffer from the evil of the efflorescence discussed, at least occasionally, though most of them very severely, as far as the lignite clays so widely extant in northern Germany are used as raw material.

Perhaps to the clay ware manufacturer it may be interesting to find that we are dealing, day by day, with a substance in our clays which up to the present time has been considered one of the rarest, and which is rarely mentioned by chemists, but which is here shown to be widely distributed though existing only in small quantities,—but what practical advantage, what money value has this knowledge? I regret that I am not in position at present to give ways and means of removing this enemy of the clay industry with absolute success. The properties of vanadium compounds have been examined less than those of the more common metals, and it is difficult to give at once a means of rendering them harmless. But at any rate by knowing the causes, opportunity is given to study the trouble in a definite direction, and I will not neglect to communicate my views in regard to the means (as far as this is possible for me to-day) which practice must use and to mention my experiments made in this direction.

It is hardly to be assumed that the vanadium compounds, be they what they may, appear only in some pieces of the product in such an unpleasant manner, because they are mixed with the clays used at random, but there is a certain justification in saying that they are considered as general constituents peculiar to the lignite clays of the plains of northern Germany. Less variation is perhaps shown in regard to the stronger or weaker appearance of the green color in different parts of the clay deposit, than is true of the separate burns in which the raw product has not been specially selected, and which in the several positions of the kiln, result in products that possess a greater or less tendency to

show efflorescence. Thus in the establishment mentioned above, green colors are found especially in the back parts of the partially continuous kiln used, while the front parts are nearly always free from them, and, as a rule, only the softer burned products are discolored. Since it is not to be assumed that only the clay containing vanadium reaches the back part of the kiln, the appearance or non-appearance of the efflorescence must be traced back to the burning process.

Since the lower oxidation compounds of vanadium on heating in air are nearly always changed to those of vanadic acid, the appearance of this strongly coloring combination must be ascribed to the action of the air. In fact the clay examined, taken from any green front brick, on being ignited at a dark red heat in the air and then placed in water, colors the latter distinctly golden yellow. This yellow coloration appears in a similar manner when the clay is burned in the trial kiln in the shape of small briquettes, the temperature being increased up to between the melting-point of silver and that of copper; that is, from 960° to 1100°. All the vanadic acid and vanadium oxide compounds are easily changed to vanadous oxide, the only insoluble compound; vanadous oxide which, on the admission of air, changes to vanadic acid, is formed by reducing influences (hydrogen, hydrocarbons, carbon monoxide) easily produced during the burning and always present in the kiln. It was now endeavored to conduct trial burns in such a manner that unburned combustible gases predominated periodically in the trial kiln in order to fix the coloring vanadium compounds by vitrification in the form of vanadous oxide. In order to make the phenomenon more striking, a clay was soaked with a strong-colored vanadic acid solution. After burning, the clay imparted an intense yellow color to water, when placed in it, if the burning temperature was too far below the melting-point of silver, 960°. However, when the temperature was increased to beginning white heat the color produced was scarcely noticeable, the clay showing incipient vitrification. From this we may conclude that during the cooling (which for the production of pure brick colors takes place in an atmosphere containing an excess of oxygen), the vanadous

oxide changes to vanadic acid, and that this does not take place, if at the incipient vitrification of the clay, the lower oxygen compound of the vanadium has fused together with the silicate.

It will now be the task of kiln builders and burners to bring about these burning conditions; and that this may be possible without any new invention appears from the fact that these conditions exist very often and that some burns or some portions of the kiln contents are perfectly free from the dreaded evil.

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### Quartz Sand in Brick Clay and One of Its Peculiar Effects

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W. H. ZIMMER, PH.D., TRANSLATOR

What difficulties are produced on changing a process of manufacture by the constitution of the raw materials used and how little these properties are anticipated owing to the imperfect knowledge of the same, is proved by a case which I had occasion to study several years ago. I was incited to a more extensive discussion by the communication of the results obtained in the investigation of Mr. C. Holthof<sup>1</sup> concerning a brick clay which showed a very peculiar behavior on being burned in a continuous kiln, and the discussion will certainly be of interest because such tender materials are also used in other places.

An extensive production of brick is carried on near Havre in France, and in the manufacture two very different raw materials are used, which furnish two entirely different products. Deposits of a very ferruginous clay, mixed with a coarse-grained sand, are found on the plateau, whose banks, 50 to 100 meters high, are parallel to the river Seine, which at this place widens like a bay of the sea. From this material, blackish blue pavers are manufactured, very similar to the Oldenburg clinkers. They are used in the extensive harbor works of the great port and are

<sup>1</sup> Notizblatt des deutschen Vereins für Fabrikation von Ziegeln, Heft 3, 1877.

also exported to Norway in large quantities as return freight for wood. In the lowlands at the mouth of the Seine there are found very extensive deposits of a tenacious material saturated with salt-water, which only recently have been raised from the sea. This place, where to-day there are quite a number of brickyards, at the beginning of the 19th century was still covered with water. The material is extraordinarily fine, but very short, has but little binding power, and shows strongly the property of silt, that is, finely-powdered but not completely weathered mineral residue, which becomes stiff when undisturbed, but becomes quite liquid on pressing and kneading.

From this material, bricks are molded in standard molds in the Flemish manner. Yellow-colored bricks are burned in very large open kilns containing 200,000 to 250,000 of the small French size, lump coal being used as fuel. These bricks are very light and tender, but are still weather-resisting enough for the mild climate of Havre to be used for the very extensive brick construction of that city.

That the material is very sensitive to a change in temperature in burning, may be seen from the fact that the lowest six and ten courses in the old kilns are always badly cracked and almost completely unfit for use. The extremely favorable results which had been produced in the burning of blue clinkers in a continuous kiln and the large losses which accompany the manufacture of these yellow bricks, brought about the erection of a large continuous kiln for burning the latter. The result of the first cycle burn was entirely satisfactory as long as the continuous kiln was moist, but the results became worse and worse when it was dried out and the burning took place at a more rapid rate. The number of bricks which were not cracked fell as low as five to ten per cent, a negative result not equaled by any other continuous kiln. The examination of the raw material undertaken for the purpose of explaining the phenomenon, showed under the microscope that for the largest part it consisted of very small, splintery and rounded quartz grains mixed with many lime shells and penetrated by branches of infusorial earth. A more extensive examination by chemical and mechanical analysis proved

that there was present only 16 per cent of clay substance (with a size of grain below 0.01 mm. diameter), and that besides the fine quartz dust and other mineral residue, 31.3 per cent of calcium carbonate was also contained in the material. In consequence of the high content of quartz which, as is known, possesses the property of increasing its volume on burning, the clay does not shrink in burning but increases in volume, corresponding to one per cent linear expansion. The low content of binding material, the looseness of structure, due to large amounts of calcium carbonate and infusorial earth, and the property of the quartz powder to expand considerably on heating, causing a tension on the interior, must be regarded as the cause of the great tenderness of the brick material in burning. The phenomena which occurred correspond precisely to these facts.

In regard to the large content of lime, it might be assumed that this would cause a bursting of the brick, due to the absorption of water after burning; this could not have been alone the cause of the trouble, because so long as the continuous kiln was wet, this should have occurred in a greater measure, but a continued destruction of the brick did not take place even after a long exposure to the air. The observation was also made that the bricks which were brought up to the maximum heat were already destroyed at a previous stage.

The kind and manner of destruction is shown by irregular cracks which are produced, especially in the sides facing the direction of the draft; they penetrate 1 to 2 centimeters deep into the brick and open up the more (often as wide as 5 mm.), the harder the clay was burned, while the core of the brick caused the brick to have the appearance of being swollen. At the same time they retained a moderate ring on being struck.

In order to determine during what period of the burn the bricks were destroyed, some of them were drawn through the firing-holes by means of tongs during the burning and during and after the cooling, being examined with the magnifying glass. It is thus shown that visible cracks appeared as soon as the bricks had reached a dark red heat and these cracks were increased to a fine, net-like system as soon as, in this condition, air was blown

upon the surface; on the other hand, those bricks which had been heated to a bright red heat so that beginning vitrification was shown by a yellow color, were not at all affected by rapid cooling. Hence it becomes evident that there was a condition of tension in the clay mass in the first stage of heating at which a large amount of quartz-powder commenced to expand, while the cementing material, the clay and calcium carbonate, had not yet softened. The effect of the change in temperature, which in the old primitive kilns was confined to the lower parts of the kiln, was repeated in the operation of the continuous kiln from one row of fire-holes to the other on account of the flow of cold air during the charging of the fuel. The bricks in those portions of the kiln, in which a rapid inflow of air always takes place during the first part of the burning, were in the condition of greatest tenderness.

On moderating the draft, carefully luting the firing-covers and narrowing the firing-holes by means of iron funnels with a small opening to allow the falling through of dust-like coal, the evil was somewhat lessened but not removed; it was removed completely only by mixing the material with 0.1 to 0.2 of plastic clay in order to increase the binding power.

This interesting material has been studied more in detail by C. Holthof. We take the following from a communication referring to the chemical changes which the clay constituents of this material undergo in burning in the presence of calcium carbonate.

The mass possessing but little binding power and being high in fine sand, in which large amounts of shell residues are often found, was first subjected to a careful mechanical analysis with the Schöne washing apparatus. There were carried over with a velocity of the current of water per second,

Between 0.10 and 0.18 mm., 24.9 per cent,  
Between 0.18 and 0.48 mm., 10.4 per cent,  
Between 0.48 and 0.99 mm., 6.8 per cent,  
Not washed out with 0.99 mm., 56.4 per cent,  
Sieved through a sieve of 0.2 mm. mesh, 1.5 per cent.

On examining these figures the low content of substance

washed out with the lowest velocity (that is, the real clay substance and a large quantity of particles which cannot be removed) at once becomes evident.

All the products of washing, on being treated with hydrochloric acid, effloresce and thus prove the presence of calcium carbonate. Under the microscope they consist in part of shells and infusoriae.

A rational analysis was made of the fine average powder, heating it with sulphuric acid for eighteen hours after a preceding treatment with hydrochloric acid for the removal of the calcium carbonate. The powder, dried at  $125^{\circ}$  which on drying lost 1.92 per cent as compared with the air-dried mass, showed the following analysis:

	Per cent.
Undecomposed residue, sand	47.88
Chemically combined silica	8.89
Alumina	3.71
Ferric oxide	1.28
Ferrous oxide	0.86
Lime	17.91
Magnesia	1.28
Potash	0.68
Soda	0.17
Phosphoric acid	0.16
Sulphuric acid	0.06
Carbon dioxide	14.39
Chemically combined water and organic matter	2.88
	<hr/>
	100.00

From these elementary figures it is seen that the mass, with the exception of a little (0.5 per cent) ferrous carbonate and magnesium carbonate, of 0.10 per cent of calcium sulphate, and 0.36 per cent of calcium phosphate, consists of :

- 46 per cent quartz sand and residue of crystalline igneous rock (feldspar, mica, etc),
- 31 per cent calcium carbonate, in the form of seashells,
- 12<sup>1</sup> per cent clay substance, and
- 9 per cent of minerals decomposed by sulphuric acid, beside organic substances.

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\* Under the assumption that the ferric oxide found replaces equivalent quan-

The sand which was removed was also examined further; it contained :

	Per cent.
Silica -	94.14
Alumina and traces of ferric oxide	3.25
Lime -	0.23
Magnesia -	0.20
Potash -	0.99
Soda -	1.90
	<hr/>
	100.00

This composition proves that large quantities of quartz are present in the mass, whose well-known increase in volume on heating evidently is the cause of the increase in the size of the bricks on burning. For the purpose of examining the chemical reaction taking place in the burning of the body, a brick made from this material was burned in a local stove-tile factory and was analyzed.

Analysis showed, in terms of the dried substance, a content of 48.91 per cent of insoluble residue, and 9.6 per cent of silica, soluble in hydrochloric acid. These figures check very closely with those from the above analysis: 47.88 per cent insoluble sand and 8.89 per cent chemically combined silica, the fluctuations being entirely within the limits in which analytical data vary even for very homogeneous materials, unless exactly the same average powdered sample is analyzed.

They show that only the silica present in the material, which is unlocked by sulphuric acid, has entered into combination with the lime, and that the quartz sand has remained virtually unchanged.

On the other hand, the silica of the clay has been changed to a condition in which it has become soluble in hydrochloric

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tities of alumina in the constitution of the clay, and that the chemical water is not partially replaced by equivalent amounts of ferrous oxide, lime, magnesia, potash, or soda, there is obtained :

4.94 per cent alumina and ferric oxide, chemically united,

5.37 per cent silica,

1.65 per cent water, giving

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11.96 per cent of clay substance.

acid, and like the alumina has united with a part of the lime present.<sup>1</sup>

A larger part of the latter, however, remains as caustic lime and to this is very likely due the cracking of the burned brick that is often observed.

If a clay higher in clay substance is incorporated with the material, there is no doubt but that this trouble would be overcome, since on burning the free lime unites with the silica as well as with the alumina of the clay, and the brick would not contain any more free lime.

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### On Barium Compounds as an Addition to Clay in the Manufacture of Face-Brick

W. H. ZIMMER, PH.D., TRANSLATOR

While the green efflorescence caused by the presence of vanadium compounds can be prevented only by very strong, and during the last stage reducing, burning of the brick, a small

<sup>1</sup> According to the experiments made in the laboratory, this union of the constituents of clay and lime took place at a low temperature, and even more completely than the combination between amorphous silica and lime. It is an interesting fact that the clay, although a basic silicate, possesses the property of uniting with bases like the fixed alkalies, lime and magnesia, at higher temperatures, at the same time decomposing the less stable compounds of these bases with acids, evidently with the formation of bisilicates in which the base replaces the water of the clay substance. This behavior of the hydrous aluminum silicate is best shown in the reaction upon the nitrates of potash and soda. At a temperature not exceeding the melting-point of lead the clay substance acts as energetically upon the nitric acid as amorphous silica does at a distinctly red heat. On removing the excess of the nitrates used with water it is found that a soluble silicate of potash or soda has not been formed, but that a compound of the clay with the potash or soda has been produced, which is difficultly soluble in water, but easily decomposed by dilute acids, and in regard to which analysis shows that the chemical water of the clay substance is replaced, according to the time of the experiment and the temperature employed, by potash or soda.

The clay substance decomposes other compounds, decomposed by free silica, with greater ease, though not as markedly as in the case cited. Thus calcium sulphate is decomposed by clay with but a weak reduction at a lower temperature than by silica, and hence the clay may well be assumed to exert an especially favorable influence in the burning of materials used for the manufacture of light-colored face-brick in regard to the production of pure colors.

addition of natural barium carbonate (witherite) to clay prevents the appearance of white efflorescence during the drying. Of late the barium chloride, which now may be obtained very cheaply on the market, is used for the same purpose. It appears to me to be important to make clear the function of the barium compounds. White efflorescence on the surface of face-brick appears only when the water in the pores, giving to clay its plasticity, contains salts in solution. The evaporation of the water during the first stage of drying takes place exclusively from the surface; the salts in solution are deposited in small crystals on the surface and fresh quantities of the saline water are brought there by the capillary attraction of the clay.

The effect of the salts, according to their nature, may differ very much. The calcium, magnesium, aluminum, iron, and sodium sulphates occur in clays in larger quantities; there are present also, as a rule, smaller quantities of chlorides or phosphates of the bases named or combinations of the oxides with acids originating from the decay of organic substances. Of these salts the calcium, magnesium and sodium sulphates are especially injurious because they segregate very easily in well-defined crystals. The chlorides are less injurious since they may be kept in solution by a very small quantity of water and in part are deliquescent, so that they cannot be deposited in the solid state in a moist atmosphere which is the rule in a brick-drying shed. The calcium sulphate is most to be feared since it crystallizes first of all the salts present, its solubility being 1 part in 450 parts of water.

Not only the sulphates present in the clay are to be feared as a source of efflorescence, but also the water used in making the clay plastic, contains considerable amounts of salts, being often a saturated solution of calcium sulphate so that it must also be taken into account. It is shown by practical observations that even very small amounts of calcium sulphate are able to produce discoloring efflorescence on the brick and that a content of 0.1 per cent may give rise to disagreeable discolorations of the surface.

Let us now see how the barium compounds added to the clay act upon these salts, and let us suppose that barium carbonate is used. Barium has the property of uniting very energetically with sulphuric acid to form a compound absolutely insoluble in water. It thus takes the sulphuric acid from the sulphates of lime, magnesia, alumina and iron, in part also from the soda, and these bases are likewise changed to insoluble carbonates and hydroxides. In this manner it causes a complete removal of the soluble sulphates and bases from the water which fills the brick, and subsequent efflorescence cannot take place.

An excess of the insoluble barium carbonate is by no means injurious; it must even be added in order that all the sulphates be removed, because the mixture of the clay with the barium carbonate can never be made so intimate that all of it becomes effective. The reaction does not take place so rapidly that an addition of just enough barium carbonate can be expected to render all the sulphates insoluble. With a content of 0.1 per cent of calcium sulphate in the clay only 0.127 per cent of barium carbonate are required, but the addition is, as a rule, increased to 2 per cent of witherite; in the case of the artificially prepared, more finely divided, but somewhat more expensive preparation, the addition may be somewhat decreased.

If barium chloride is used the amount of the addition must be decreased considerably. Barium chloride is a salt very soluble in water, which, when dissolved in water, is easily carried to all particles of the clay and can exert its action immediately. But it will be necessary to work more carefully with it. Though barium chloride precipitates all of the sulphuric acid, its place is taken by soluble chlorides of calcium, magnesium, and aluminum, which, being very soluble, may appear after a long time on the surface as efflorescence, and hence large quantities of these salts must be avoided. At the same time any excess of barium chloride must be avoided, since it, like the other salts, would appear on the surface, crystallizing there and becoming noticeable after the burning, it being partially decomposed forming a barium silicate. In this case it will always be necessary that the required amount of barium chloride for the clay,

as well as the water, be determined analytically in order to avoid an excess. For a content of 0.1 per cent of calcium sulphate (or other sulphates) in the clay and water, an addition of only 0.17 per cent of crystallized barium chloride must be taken. An excess behaves similarly to calcium sulphate, but not so energetically. This method may seem to be less suitable on account of the analysis to be made and the variations which may occur in the content of sulphates in the clay and water; still with a low content of sulphates this method is not to be underrated on account of its cheapness. However, if much calcium sulphate is in the clay, being present, both in solution and in the form of larger crystals, sometimes so much barium chloride would have to be added that the amount of the soluble salts formed would increase very much, and accordingly the object of this treatment, the removal of the efflorescing salts, would not be attained. In such a case it is always better to use the barium in the shape of the carbonate, because in this way only a small part of the calcium sulphate (that dissolved in water, but not that existing in the clay in the solid state) enters into the reaction. Since here an excess of barium carbonate is required, it will not be necessary always to consider the content of calcium sulphate in the tempering water which varies with the season.

The addition of the barium preparations does not promise any success in the treatment of efflorescence due to other salts than sulphates, which, however, are much less dangerous. The barium compounds will not be able to act upon those kinds of efflorescence which are produced by the action of the fire-gases during the burning, owing to careless water-smoking. The effect of the sulphuric acid developed from the sulphur of the fire-gases extends only to the surface and not to the interior of the brick, and again its quantity is so large that the small amount of the barium contained in the clay would have no appreciable effect upon it. The addition of barium can only react with those salts which are present in the clay on drying, and only with the sulphates.

## The Conditions of Density of Molded, Re-Pressed and Dry- Pressed Clay and the Effect of Composition upon the Density of Clay Bodies

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ALBERT BLININGER, B.S.C., TRANSLATOR

The main object in view in the manufacture of many kinds of clay ware is that the product be as uniform as possible in shape and size, especially when it is to be used for extensive, uniform surfaces, with regular thin joints, *i. e.*, brick fronts, floors, and paved walks. The raw material of the clay worker offers the greatest difficulties in this direction, since he cannot produce from it directly, as with other materials, the pieces in the desired sizes by molding, but must remember that they change their shape, as well as their dimensions, during manufacture. The manufacturer is rather helpless in regard to the control of these changes and the maintenance of exact measurements, for the changes are by no means so constant that he could estimate the success of his work.

The difficulties are founded in the property of the clay to swell on contact with water and again to shrink on the evaporation of the latter. Even if in the drying of clay such circumstances are removed as much as possible, which beside a decrease in dimension might also bring about a warping of the shape (a condition which is attained in well-equipped plants with more or less success), still there are always left enough difficulties in regard to the retention of the shape and dimensions in the process of burning. Warping may be avoided more or less by using the clay as stiff as possible, varying with the shape and weight of the pieces (so that they are not deformed by their own weight), and again by taking precautions that the ware does not become crooked or cracked owing to one-sided rapid drying. Every dried mass of clay contains a greater or smaller volume of pore space, according to the composition of the body, its fineness, and the manner and method of molding. This volume of pore space is increased in the first stage of burning, since several of the con-

stituents of clay are volatilized. These are the chemically-combined water and organic substances as well as the carbon dioxide in calcareous clays. It is the object in burning the clay, not only to take away its property of softening on absorbing water, which is only attained by the expulsion of the chemically-combined water, but also to make it dense and to harden it by partial vitrification, so that it may be enabled to withstand the influences of the weather and mechanical abrasion.

The highest degree of resistance of clay wares to the influences named is reached when vitrification has been carried so far that the pore spaces of the clay are closed by an extensive softening of the mass, which thus becomes impenetrable to water; the separate constituents are so fused into each other that the fracture assumes a glassy or stony character. This degree of vitrification is always required in porcelain, in stoneware, and such clay wares which are subjected to a strong mechanical abrasion like clinkers, floor tiles and paving brick. In all these products, the decrease in volume brought about by burning must, in general, be equal to the pore volume existing after the first stage of the burn. It now becomes obvious that the difficulties in burning, of maintaining definite dimensions, in such products, will be the greater the greater the shrinkage in the two processes named, that is, the greater is the quantity of water required in molding for making the mass workable, and the greater the pore space, which on the one hand remains after the drying of the clay, and on the other is produced by the volatilization of several constituents during the first stage of the burning. The magnitude of the shrinkage in burning is a function of the ratio of the pore space to the outside dimensions of the piece when the temperature has been raised to the point at which the pores are closed completely.

The first part of the shrinkage which takes place in drying may be controlled to a certain extent in its effect upon the maintenance of the proper shape, and during drying certain corrections are still possible in regard to shape. These may consist of covering wet pieces of clay with burlaps, thus preventing the rapid drying of some parts especially liable to warping and

enabling the parts in which a slower evaporation of water takes place, to keep step with the others in drying; or, again, after the most rapid shrinkage has taken place, when the clay still possesses slight plasticity, the shape may be corrected by re-pressing, by the use of templates or similar appliances.

The deformations which are produced during the drying cause a loss only of the work expended in molding and drying, while the material itself may again be used. The conditions are different, however, in the shrinkage which takes place during the burning. This is beyond any control or correction and does not only cause a loss of all the cost of labor expended upon the ware so far, but also of the cost of material and coal inasmuch as the warping due to burning may give rise to waste or low-grade products. For this reason the manufacturer must not only see that the shrinkage in drying is reduced to a minimum but also that the clay after completed drying has already become as dense as possible because only in this way is it possible to decrease the burning shrinkage.

The obvious remedy on hand would be to decrease or to remove entirely the drying shrinkage by reducing the amount of water required for softening the clay in plastic molding, or by neglecting the plastic properties of clay as far as the shape of the products will permit, and to use powdered dry clay which, under a high pressure, is united to a compact mass.

Both ways have been followed on a large scale, the latter with a decided success in retaining the shape up to the beginning of burning. Views are very much divided, however, in regard to the way bodies can be produced that show least warping in burning, when dealing with a complete vitrification of the mass; or in other words, as to how bodies are obtained which possess maximum density before burning and hence shrink least after burning. Since positive investigations along this line do not exist, it might be of general interest to communicate a few experiments made in this direction.

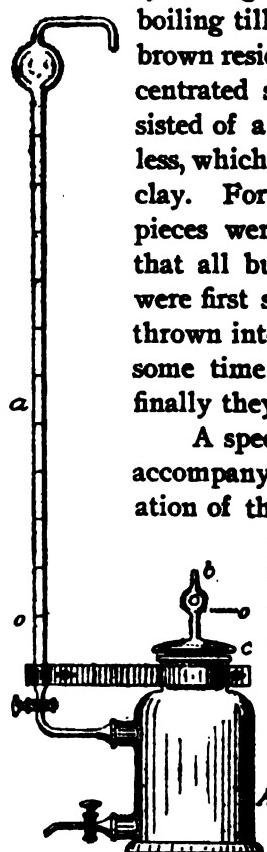
Two clays were used in this investigation which are used in the manufacture of clinkers which possess similar chemical and physical properties and are widely distributed in northern

Germany. Both clays come from near the Finow Canal, from Heegermuehle. The one is a calcareous, diluvial clay and is used in making buff-colored common brick and face-brick which at a temperature exceeding the melting-point of gold are changed to green clinkers with a considerable shrinkage. The second is a clay low in lime and high in iron; it is located above the first, and at a somewhat lower temperature gives clinkers of a dark reddish brown color which shrink less in the fire and stand up better in the kiln. Both materials are used in the finely washed condition. The figures given in the accompanying tables show the conditions of density of these clays alone, and also of mixtures of the same and with powdered clinker, as grog, and quartz sand, both used in sizes of grain up to 1 mm. in diameter.

The clays as well as their mixtures were thoroughly dried, powdered and pressed into tiles, 15 cm. square and about 1.5 cm. thick, on the hydraulic press of the Royal Porcelain Factory, used for making floor tiles. These were cut, in three cuts, into six approximately equal parts, the cut surfaces being trimmed neatly in order to avoid crumbling; 3 parts were retained for determining the porosity in the thoroughly dried and in the burned condition. The other 3 parts were softened in water and from this mass briquettes 6.6 cm. long, 3.3 cm. wide and 1.5 cm. thick, were molded in a bronze mold by pressing with the hand and shaving off the excess. Of these, half of them were immediately dried in the air, the other half re-pressed in the leather-hard condition in the bronze mold by giving a few light taps with the hammer on a stamp fitting into the mold till the edges were perfectly sharp. A part of the red burning clay was spread out thinly and placed in a cellar; it thus absorbed 9.5 per cent of water from the air, felt damp to the touch and could be balled together somewhat by hand. From this material a few tiles were also made on the hydraulic press, once under the full pressure of the press and again using only the larger of the two pressure pumps.

The determination of the porosity of the clay bodies molded under the different conditions, was accomplished by direct measurement of the raw as well as the burned test pieces in such

manner that the exterior volume was determined, and also the amount of indifferent liquid which was taken up on the complete saturation of the clay. For this purpose there was used for the unburned clay heavy petroleum of 0.805 specific gravity, obtained by freeing ordinary petroleum from the light oils by boiling till its boiling-point had risen to  $180^{\circ}$ . The brown residue was decolorized by shaking with concentrated sulphuric acid and caustic soda, and consisted of a clear blue opalescent liquid, almost odorless, which was completely indifferent to the unburned clay. For the determination of porosity the burned pieces were saturated in water. In order to be sure that all bubbles of air had been removed, the pieces were first saturated completely with alcohol, and then thrown into boiling water and allowed to boil in it for some time till all the alcohol was evaporated, and finally they were allowed to cool under water.



A specially constructed apparatus, shown by the accompanying illustration, was used for the determination of the volume of the test pieces. This consists of a glass bottle, A, holding about 1 liter, which is provided at the side near the bottom with a glass cock, and above the latter with a projection which is connected with a burette, a, containing 50 to 60 cc. and divided into 0.1 cc. The wide neck c of the bottle, which serves for the introduction of the test pieces, is 5 to 6 cm. wide and can be closed by a well-ground glass stopper, hollowed out at the bottom. This glass stopper is provided with an opening into which a thin glass tube, b, is inserted, and which on top is provided with an open bulb. This tube has a mark etched on it which is at the same level with the zero point of the burette a. To the upper end of the burette, which is drawn out to a thin tube, a rubber tube is attached which may be closed by a pinch-cock.

In order to determine the volume of a clay body in this ap-

paratus the latter is first filled with boiled water or on measuring unburned bodies with heavy petroleum in such a manner that the liquid reaches the two zero points in the tubes *a* and *b*. Any air bubbles are to be removed by inclining the apparatus, collecting the bubbles in the hollow of the large glass stopper, and exhausting them through the tube *b*. The addition of liquid takes place through the small tube *b*, the removal through the lower cock. The apparatus being ready the burette *a* is filled completely by suction through the rubber tube and kept filled by closing the pinch-cock. The wide neck *c* is then opened, and the test piece, which before has been saturated with water or petroleum and has been dried superficially, is thrown in. After closing the neck *c*, and opening the pinch-cock just a little, so much liquid is allowed to run from the burette into the bottle *A*, that after the expulsion of all air bubbles, the liquid rises to the zero point of the tube *b*. The volume of liquid which has been displaced by the body is then found in the burette *a* and it can be read off directly. For further determinations so much liquid is to be removed through the cock without removing the test pieces previously used, that the level in the burette again stands at zero, and after drawing up the liquid in the burette a second test piece may be thrown into the bottle. This may be continued so long as the bottle *A* can hold new test pieces; then the apparatus is emptied.

In this manner the pore space of a piece of clay is obtained expressed in per cent and referred to the exterior volume without making a determination of the specific gravity of the clay necessary; this representation is decidedly more instructive than that of referring the pore space to the volume of the water absorbed, and expressing it in terms of the weight of clay, which has been practiced in the work of Dr. Aron, Olschewsky and myself. If *V* stands for the exterior volume of the piece of clay to be examined for porosity, *g* the weight of the petroleum absorbed, and *s* for the specific gravity of the petroleum, then the porosity expressed in per cent of volume is

$$P = \frac{\frac{g}{s} \cdot 100}{V} .$$

The determination of porosity in this manner contains at the same time the elements for determining the specific gravity of the clay. If  $G$  is the absolute weight of the clay test piece before saturation with water or petroleum, then the specific gravity is calculated by

$$S = \frac{G}{V(100 - P)} \cdot \frac{100}{100}$$

The clay test pieces made in this manner by different methods of molding show the following porosities in percentage by volume of the test pieces used. The different mixtures mentioned in the table were kneaded in the soft condition, dried, and again powdered.

Method of molding.	Hegermann's clay, burning hot	Hegermann's clay, burning red	clay 1 part H. buff clay + 1 part H. red clay	clay 1 part H. buff clay + 1 part H. red clay	clay 1 part H. buff clay + 1 part H. green from cylinders	clay 1 part H. buff clay + 2 parts H. clay from cylinders	clay 1 part H. buff clay + 2 parts quartz sand
Molded soft - - -	27.2	23.9	26.2	21.8	19.4	17.9	
Molded soft and re-pressed when somewhat hardened - - -	25.4	23.7	24.4	21.4	18.2	16.3	
Pressed perfectly dry - - -	32.1	24.9	25.4	23.2	23.1	22.6	
Pressed damp, full pressure - - -		19.9					
As before, half pressure - - -		20.2					

From this it is seen that the view that much denser bodies are produced by pressing perfectly dry clay in a hydraulic press than is possible by other methods of molding is by no means true. In the examples at hand the clay bodies pressed from dust-dry clay on the hydraulic press, with a single exception (No. 3) in which the differences are by no means large, are much more porous than those molded in the wet condition. On the other hand, the use of moist clay on being molded by hydraulic pressure, gives rise to a considerable increase in the density of the mass. But the practical use of a clay so slightly moist that

it has no real plastic property, and hence but a minimum drying shrinkage, is opposed by the fact that clay bodies with a certain small content of moisture can be converted to a fine powder only with difficulty, while with a perfectly dry clay this is accomplished more easily.

The increase in density which is caused by repressing in the leather-hard condition, is rather small compared with the wet molded clay, as is to be expected for theoretical reasons. The action of repressing consists essentially in producing or reproducing exact shapes with a clay containing only so much moisture that there is no further appreciable decrease in volume by drying and in removing air spaces caused by enclosed air bubbles, which in the wet molding are removed from the clay only with difficulty.

The behavior of the same pieces on burning is hardly less interesting than the effect of molding upon the porosity of a raw clay.

Of each of the clay mixtures given in the above table, a portion of a dry-pressed tile made from them was placed upon a fire-clay slab, and six of these slabs, each carrying a series, were distributed in the biscuit burn of a gas kiln in one and the same pile of saggars so that each was subjected to a different temperature. For this purpose a series of tests was set directly beneath the arch, another on the kiln floor, and the others were distributed in vertical intervals of about 30 cm. The temperature which existed beneath the arch of the kiln (down draft) was that of beginning bright white heat, at the kiln floor something above the melting-point of silver. Assuming that these temperatures are approximately from  $1250^{\circ}$  to  $1000^{\circ}$ , and the heat is supposed to decrease uniformly from the top to bottom within these limits, there would correspond to every series of tests an increase of temperature, from the bottom to the top, of  $50^{\circ}$ . In reality these temperature differences, however, were somewhat less since the difference between top and bottom has been estimated somewhat too high. The porosities, which are shown by the trials after burning, are given in the following table :

Burning temperature	Porosity in per cent by volume				Pressed perfectly dry				Degree of burning of the soft molded Heegermeile clay	
	1. Heegermeile half clay		2. Heegermeile red clay		Pressed damp		Pressed perfectly dry			
	Molded wet	Pressed perfectly dry	Pressed perfectly dry	Half pressed	Half pressed	Part buff H. clay	Part red H. clay	Part buff H. clay		
						-	-	-		
A. 1000° C	33.1	38.2	19.3	16.8	17.7	29.9	26.2	25.5	29.2	Soft to medium burn
B. 1050°	29.0	35.7	16.2	11.9	14.3	22.1	21.1	22.2	28.6	Burned hard
C. 1100°	1.0	18.1	9.2	4.3	7.0	1.3	4.3	10.1	28.2	Yellow-green clinker
D. 1150°	0.0	0.2	2.4	2.2	2.5	1.0	2.1	1.8	23.6	Edges rounded
E. 1200°	melt.	melt.	2.4	3.0	2.4	melt	melt	melt	21.2	Melted to a flat mass
F. 1250°	melt.	melt.	2.1	2.1	2.4				15.5	

On comparing the figures of this table with those of the preceding one, it will be seen that all the tests which contained as a constituent the calcareous clay from Heegermuehle, show a large increase in porosity at the lowest temperature used. This can be explained by the loss of the chemically-combined water and the carbon dioxide. In the ferruginous clay (2) such an increase in porosity without doubt has also taken place at a lower temperature, but this has already been more than balanced by incipient vitrification. But what is the most striking fact in this table, is the different behavior in the stages of increasing density. In the calcareous material (1) the density increases very rapidly within a temperature interval of  $50^{\circ}$ . The manner of molding as well as the presence of admixtures, which shrink less or not at all, may retard the rapid shrinking somewhat but at any rate this retardation does not equal that which takes place in a material, free from lime, and which extends over several hundred degrees.

The cause of the rapid shrinking of the calcareous clays is to be sought in the fact that the lime contained in it becomes

chemically active only at a higher temperature ; but then it exerts its fluxing action very rapidly, while in a clay free from lime such an energetic action cannot take place. The same phenomenon, however, appears also in other bodies. An experienced porcelain manufacturer, having had occasion to work several porcelain bodies together at the same time, has informed me from his practice that when porcelain contains marble as a flux the increase in density commences at a higher temperature than in the case of a large addition of feldspar, but nevertheless the pores are closed completely, and transparency is attained at a lower temperature with the first than with the second. This behavior is worthy of notice for many branches of the clay industry in which it is desired to produce very dense and hence always strongly shrinking products in regular shapes, for it is evident that aside from the absolute magnitude of shrinkage, the rate at which it takes place must also be of extraordinary influence upon the retention of a regular shape.

In what inner connection the density of clay stands to the chemical composition and inner structure, has so far not been determined, at least not for more impure and coarser materials, since the conditions are extremely complicated owing to the varying constituents which cannot be separated and examined in regard to porosity. In order to obtain some clearness in this direction it seems advisable to start with pure and well-defined bodies, and to discuss, with the help of these, the questions : First, what effect has the proportion of clay substance to the non-plastic constituents ? and second, what influence does the varying constitution of the clay substance exert upon the density ? In order to come nearer to the solution of these questions, two series of bodies were prepared whose corresponding members possess the same chemical composition, but in which in the one case the cementing clay substance was a pure, but "short" kaolin, and in the second, a very plastic clay.

The composition of these series was as follows :

	Per cent							
	1	2	3	4	5	6	7	8
Clay substance ( $\text{Al}_2\text{O}_3$ , $2\text{SiO}_2$ + $2\text{H}_2\text{O}$ ) -	25	30	35	40	45	50	55	60
Feldspar ( $\text{K}_2\text{O}$ , $\text{Al}_2\text{O}_3$ , $6\text{SiO}_2$ ) -	20	20	20	20	20	20	20	20
Quartz ( $\text{SiO}_2$ ) -	55	50	45	40	35	30	25	20

In the series designated by *A* the clay substance was introduced by kaolin from Pilsen, and for the series *B* by the plastic clay from Ebernhahn, near Coblenz. The composition of these clays was as follows :

	<i>A.</i> Kaolin from Pilsen Per cent	<i>B.</i> Clay from Ebernhahn Per cent
Clay substance - - -	94.89	75.23
Feldspar - - -	2.21	
Quartz - - -	2.90	24.77

From these figures the quantities of clay (or kaolin), feldspar, and quartz, required for the desired composition, were obtained by calculation.

Feldspar and quartz were ground into an impalpable powder, in the condition in which they are used for the making of bodies and glazes in the manufacture of porcelain.

The two series, though possessing the same chemical composition in their corresponding members, differ widely in physical properties, corresponding to the different properties of the clay substances used.

The bodies of series *A* are "short," even in the members highest in clay substance, and dry to a friable, strongly chalking mass. The bodies of the series *B* are still very plastic, and dry to a hard mass, which chalks but little even in the members containing the greatest amount of non-plastic matter. Those highest in clay, on scraping with the finger-nail, show a smooth, polished surface, while even those highest in clay of series *A* remain dull and chalky.

The briquettes made from the 16 body mixtures of the series

*A* and *B* were examined for porosity in the manner described above and were :

1. Dried in the green condition at 120°.
2. Burned to the melting-point of silver, 960°.
3. Burned to beginning white heat, 1200°–1300°.
4. Burned in the porcelain glost-burn, at the melting-point of wrought iron, about 1500°.

The burning was done with the same briquettes in turn, always two at a time, all the test-pieces being burned in the same saggar.

The test-pieces were molded wet in a bronze mold and then re-pressed in the leather-hard condition till the edges were all sharp.

The results of the porosity determinations, together with the respective shrinkage measurements, are collected in the following tables :

A. CLAY SUBSTANCE DERIVED FROM THE PILSEN KAOLIN

	1	2	3	4	5	6	7	8
Porosity, raw -	33.6	36.0	36.0	37.6	37.8	38.2	38.6	38.8
Porosity at 960° -	33.8	36.2	36.2	37.7	37.4	38.2	38.5	39.0
Porosity at 1300° -	1.0	1.8	1.9	2.6	1.7	1.7	1.5	2.6
Porosity at 1500° -	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Linear shrinkage 950°	0.0	0.0	0.2	1.5	0.7	0.9	1.3	1.7
Linear shrinkage 950°–1200° -	10.7	11.7	11.7	11.7	11.5	11.6	11.3	11.2
Shrinkage, 1300°–1600° -	2.3	1.2	1.3	1.0	0.9	0.2	0.2	0.3
Total shrinkage -	8.4	10.5	10.4	10.7	10.6	11.4	11.5	11.5

B. CLAY SUBSTANCE DERIVED FROM THE EBERNHAHN CLAY

	1	2	3	4	5	6	7	8
Porosity raw -	26.6	26.9	27.4	28.3	28.2	28.3	29.7	29.8
Porosity at 960° -	28.2	27.2	27.6	28.1	26.2	25.9	26.2	25.1
Porosity at 1200°–1300° -	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Shrinkage at 950° -	0.2	0.6	0.5	1.2	1.7	1.9	2.3	2.6
Shrinkage, 1200°–1300° -	7.7	7.4	7.7	7.1	6.8	6.4	6.1	6.0
Total shrinkage -	7.9	8.0	8.2	8.3	8.5	8.3	8.4	8.6

In the porcelain glost-fire all the trials were bloated.

If the results of the first horizontal columns are compared with each other, a definite regularity will be observed, inasmuch as the density increases in the unburned bodies with an increasing content of non-plastic materials, though this is shown only by slight differences.

In the second horizontal column the porosity in the bodies containing kaolin has remained unchanged, notwithstanding the loss of chemically-combined water, while in the bodies containing plastic clay a slight increase in density, but distinctly noticeable, appears especially in the briquettes containing less of the non-plastic materials.

This is a striking fact, inasmuch as the kaolin used, as well as the plastic clay, belongs to the refractory materials since the feldspar, the most easily fusible of their constituents, does not show the slightest indication of softening, at the low temperature to which the tests of this column were exposed (the melting-point of silver). Hence, at this temperature, an increase in density must have taken place, which in the trials *A* is equal to the loss in volume brought about by the expulsion of the chemically-combined water, and in the trials *B* even exceeds this somewhat. This increase in density is also shown by the slight, but definitely determined, linear shrinkage of the briquettes. This shrinkage is the greater, the higher the content of clay substance in the clay, and hence must be caused by this constituent.

According to this the assumption made heretofore by a number of investigators, especially by Olschewsky and also by myself, that the shrinkage of the clay is due to an incipient softening, to the capillary absorption of the fused constituents, is not tenable, at least not at the relatively low temperature at which clay loses its chemical water, though this assumption may apply to the higher temperatures at which undoubtedly a partial fusion takes place. This first shrinkage may find an analogy in the shrinkage which many bodies undergo when suffering from chemical decomposition, leaving behind solid and infusible constituents. Of such there might be named calcium carbonate, magnesium carbonate, aluminum hydroxide, and many others, which, on losing carbon dioxide and water, likewise shrink con-

siderably, although the substances left behind (lime, magnesia, and alumina) are considered absolutely infusible. This increase in density can be explained only by a movement and a denser crowding together of the molecules simultaneous with the loss of water and carbon dioxide or taking place later, without, however, assuming a partial liquefaction in the ordinary sense.

It seems to appear from the figures obtained, that the contraction of the clay mass so caused, takes place more energetically or at a lower temperature in the presence of a clay substance with pronounced plastic properties than with the less plastic clay substance of kaolin. At the temperature of melting silver, the mixtures highest in clay of the plastic type have already become the denser ones, while the corresponding mixtures with kaolin clay substance, like in the raw condition, have here also remained more porous.

As the temperature, to which the trials of the third horizontal column were exposed, has become sufficiently high to soften one of the constituents of the bodies (the feldspar), a maximum density, or nearly a maximum, is attained, and the shrinkage thus also reaches its maximum. At a still higher temperature, in the glost-burn of the porcelain kiln, a negative shrinkage was observed in the briquettes made from the kaolin; that is, an increase in volume, which becomes especially pronounced in the trial pieces high in quartz, and is due to the known property of the quartz to increase in volume when changing at a high temperature from the crystalline to the amorphous condition. This also coincides with the investigations of H. Rose, according to which the specific gravity of the porcelain decreases with an increasing temperature. The expansion measured in the work under discussion is simply another expression for this observation, for a decrease in specific gravity can be explained only by an increase in external volume, an increase in the volume of the pore space being excluded in the case of transparent porcelain. And we are dealing here altogether with porcelain compositions.

In the trials *A*, whose clay substance is derived from the plastic Eberhahn clay, the expansion could not be measured, since it was bloated and deformed in places.

The total shrinkages correspond entirely to the pore space contained originally in the green as well as the soft-burned trials.

The differences in porosity, due to the different physical constitution of the hydrous aluminum silicate, are more striking than the difference in porosity caused by the proportion of the clay substance to the fine non-plastic matter not containing any water. While within the tables *A* and *B* the fluctuations in porosity amount only to a few per cent in volume, they increase very much when the corresponding bodies of the two columns are compared with each other. With the same composition the trials made from the plastic clay substance are much denser in the green condition than those produced from the kaolin clay substance, and the total shrinkages are hence much greater in the plastic clay briquettes with a correspondingly greater tendency to deformation.

As far as conclusions can be drawn from this investigation, they may perhaps be formulated as follows :

1. The shrinkage of clay bodies of a given composition in burning is dependent upon the ratio of the pore space existing after drying or produced at a low temperature, owing to volatilization, to the external volume.

2. The greater the shrinkage (*i. e.*, the pore space), the greater the danger of deformation.

3. With equal pore space and equal shrinkage the tendency to deformation is the greater the more rapidly, or within the smaller a temperature interval, the pores are closed.

4. The density of raw clay bodies is determined by the kind and manner of molding. The greatest density is attainable by subjecting damp clay to a great pressure; next to this comes the re-pressing of molded pieces in the leather-hard condition, followed by wet molded briquettes. The most porous structure is obtained by pressing, mechanically, entirely dry powdered clay, even under the greatest practical hydraulic pressure.

5. The porosity, and hence the shrinkage of clay bodies in fire, becomes the smaller the greater the amount of non-plastic constituents is as compared with the amount of fine particles of clay substance not removable by washing.

6. Under otherwise equal conditions the porosity, and hence the shrinkage on burning, is the smaller the more the binding clay substance approaches in its properties the plastic, soapy clays, and it will be the greater the more it possesses the "shortness" of the kaolin clay substance.

7. Shrinkage begins at a lower temperature for those bodies whose clay substance possesses distinctly plastic properties than for those which contain a kaolin-like clay substance.

8. The fusibility is not the only factor governing the temperature at which the shrinkage of the clay begins.

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### What Properties Must a Clay Possess in Order to be Especially Suited for the Manufacture of Clinkers<sup>1</sup> and Paving Brick?

ALBERT BLEININGER, B.S.C., TRANSLATOR

The question referring to the best materials and the best method of manufacture of clinkers and thoroughly vitrified bricks, which are to be used for the paving of floors and streets, has been brought up very often, and different views have been expressed as to the suitability of the one or the other material. Owing to the lack of sufficient scientific investigations touching upon this subject, it must first be remarked that the clay must soften gradually in the fire, must not lose its shape, and must change its volume during the drying and burning within as narrow limits as possible. But to satisfy these requirements a number of different conditions are necessary in regard to the composition of the material from the chemical, physical, and molecular aspect.

It has been said, based on the experience of practice, that the red clays are best suited for clinkers, and others claim that the yellow burning calcareous ones are best, because they

<sup>1</sup> Clinkers is the name by which the dark-colored usually bluish black paving bricks are designated both in Germany and England.

contain the largest amount of flux and vitrify easily at a low temperature.

It is known that there are quite a number of materials which possess widely different properties and which may be used for clinkers. Choosing the specially characteristic properties there are two which require our special attention. The constituents of the clay must be so put together that the one part fluxes at as low a temperature as possible, forming, so to speak, the igneous cementing materials for the other, non-fusing parts; on the other hand there must be present a portion which must be as refractory as possible and attacked as little as possible, chemically, by the easily fusing portion, and which must be present in sufficient quantity to form a skeleton, which holds together the softening mass and prevents the complete change to a viscous mass. The residues of feldspar and augite, which are often found in a clay, are as a rule the most fusible constituents; then comes the clay proper, which sometimes is so fusible that it may serve as a flux, and again often very refractory, when it helps to retain the shape. Finally we have as a constituent of clay, the quartz which assists in maintaining the skeleton. All data are lacking in regard to the proportion in which the fusible and the more refractory constituents of the clay must stand to each other for best results; very likely, however, this ratio must be similar to that of porcelain, where the fusible constituents as a rule amount to from one-fourth to one-third of the whole.

Another important point is that a brick must show as small a shrinkage as possible, and in this respect we must examine the factors of this shrinkage. Two kinds of shrinkage are to be distinguished, the one which takes place in drying, the other in burning. The difficulties which are produced by the shrinkage in drying may be overcome with comparatively little trouble. We may reduce shrinkage to a minimum by working the clay as stiff as possible; we may straighten crooked brick by re-pressing; or if we disregard the plasticity of the clay, we may mold it to the desired shape in the dry condition by hydraulic pressure. It is much more difficult to control the shrinkage of

burning. The shrinkage in burning is the greater the larger the pore space is in the clays after drying, for vitrification is nothing else than the complete closing of the pores which are produced in drying, as well as in burning, by the volatilization of several constituents. The difficulties of retaining the exact shape of the ware are the less, the fewer pores the clay contains after drying; that is, the denser it has become in molding. The volume of these pores depends essentially upon the physical condition of the separate constituents of the clay. From earlier investigations, which were published in the *Notizblatt* and other technical journals, the effects of finer or coarser sand, fine or coarse grains of grog upon the density of the clay, are known.

Another factor which so far has not been considered, is the character of the real clay substance acting as the cement which perhaps has a still greater influence upon the density of the clay than the non-plastic substances which are mixed with the clay by nature, or artificially. We may distinguish two different modifications of clay-cementing material whose physical properties differ from each other, namely, the clay substance of the kaolin and the clay substance of the fat, heavy, plastic clay. Both cementing materials are chemically identical; the differences between them are not any greater than between the separate members of the same class; in their physical properties, however, they are very different. The clay substance contained in the kaolin dries to a soft powder-like mass, while the clay substance of the same chemical composition, which is contained in the plastic clay proper, dries to a horn-like mass. The pore spaces which remain on drying of the clay correspond to this different behavior. The clays which contain kaolin clay substance as a binding material, or a clay substance which approaches in its properties those of the kaolin, are much looser in the presence of the same amount and character of non-plastic matter than such which contain the horn-like variety of clay substance. The linear shrinkage may vary very much with otherwise the same chemical composition accordingly as the cementing substance is derived from a plastic clay or a kaolin. I had an opportunity to observe this with bodies which contained equal

amounts of quartz-powder and feldspar ; the porosity in the air-dried condition varied from 26 to 39 per cent by volume, according as the binding clay substance was derived from a plastic or a kaolin clay. From this it is seen that for the manufacture of clinkers one should look as much as possible for such clay substances which dry to a hard mass ; one must avoid the kaolin-like bodies, and use as much as possible the horn-like variation. In using a very plastic clay substance, one is also enabled to increase the amount of non-plastic matter to a very high percentage without reducing the working quality of the body. A very high content of non-plastic matter, however, increases the density essentially.

But where can the manufacturer obtain the most suitable materials for the manufacture of clinkers when he is restricted to a certain clay bed? Not every one will be in position to obtain such a material and to manufacture clinkers. But if one has in his clay bank, layers of different appearance and of different properties, he may determine by suitable tests which materials are relatively the best for the manufacture of clinkers; and he will find that those are the most suitable which contain the most clay binding material but at the same time remain workable and contain the non-plastic matter mixed with it in a state of as fine a division as possible so that it cannot be distinguished by the eye from the clay itself. In other cases it will be possible to make use of other materials. It must always be the main consideration to take clays which do not contain kaolin-like clay substance, but clay as plastic as possible. I want to return to this point at this opportunity since at the last convention of the Society for the Manufacture of Brick, Clay Wares, etc., much was said in regard to the suitability of calcareous materials for the manufacture of clinkers and because we possess a few materials quite suitable for the purpose.

In the calcareous clay used for the manufacture of clinkers, though the brick may be very dense after drying, a loosening of the structure is brought about by the expulsion of the carbon dioxide. The use of calcareous material will, however, not be excluded when the non-plastic matter contained in it is ex-

tremely fine in character and the clay substance is so plastic that its quantity may be reduced to the smallest possible amount. For this reason I believe that in many places of northern Germany the very fine silt-like brick clays may be made into a good clinker material by the addition of very plastic clays from the Lausitz. It will perhaps be possible in many places to obtain lignite clays which are found in the Lausitz and in the province of Saxony, at prices which would permit of a mixing of the limy clay. A second source, as far as northern Germany is concerned, would be the North. In Sweden, as well as upon the Island of Bornholm, we find beautiful deposits of plastic clays. These deposits may perhaps become important for brick plants which, owing to their location on the Baltic Sea, may obtain transportation from those places.

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### Note on Glazed Building Brick

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PROFESSOR EDWARD ORTON, JR., TRANSLATOR

The question of the resistance which glazed building brick offer to the weather, has been already touched in a previous chapter, "On the Influence of Sulphurous Coal on Clay Ware." In the case at hand (which suggested this discussion of the subject) we have to deal with a soft-burned red brick, having a fine structure, and apparently having been burned from a smooth or "fat" clay. The cuprous lead glaze which it carried was not intimately combined with the brick, and could be easily detached by means of a knife. The uppermost layer of the brick, however, generally remained attached to the glaze. The layer of the body directly under the glaze seems to have been loosened by the action of the weather, and the question arises, how is it possible for this loosening to occur, and also, by what means can it be averted?

First, it must be stated, that all stone materials in this cli-

mate are exposed more or less to destruction through frost. This is due to the fact that water has the power of expanding considerably at the moment of freezing, and this increase of volume amounts to about one-ninth of the volume of the water present.

If, now, the water in the brick freezes, a considerable pressure is exerted on the walls of the pores, and if they of themselves can sufficiently withstand this pressure, the ice formed must be forced out of the pores as little rods of ice. These are the smaller in diameter, according as the brick is closer in grain; in coarse sandy clays, they are thicker, corresponding to the width of the pore openings, and often extend up as much as 1 cm. from the surface of the brick.

Ice expands on freezing, and when under a strong pressure is forced through a fine opening, like a rod. This can also be asserted of many metals, especially lead. If it did not possess this property, every brick, even the most solid, would be demolished without fail, by the freezing of the water in its pores.

If now, taking advantage of this porosity of bricks, we allow them to become saturated with water, which is desirable in building, we must also be sure that ice can escape from them. Bricks, in which coarse sharp sand has been used to reduce the plasticity of the natural clay, allow this ice to escape easier than bricks made from an even, fine-grained material, simply because, in the first case, the pores are of a greater diameter.

With equal hardness of burn, or rather, with equal resistance of the pore walls, the demolition of the structure will increase in direct proportion as the diameter of the rods of ice which have to be expelled from them decreases, which is the same as saying, in proportion as the pressure on the pore walls increases.

For this reason, we see in medieval buildings, in northern Germany, which are often decorated with glazed bricks, that precisely those bricks have endured best the waste of centuries, whose clay substance has been reduced in plasticity by the coarsest, sharpest sand, and which were thus able to permit the expansion of the ice formed in freezing, without necessitating the expulsion of the same from the mass of the brick. In fact,

they were provided with such a large amount of hollow spaces, that they furnished sufficient room for this expansion.

We also observe that otherwise good building brick, which will stand the action of frost while in an unglazed condition, will commence to succumb to its action after a few years' exposure, when covered with a glaze. As an example of this, I would point to the piers of the Alsen bridge at Berlin, where the glazed portions have already required renovation, while the unglazed portions, made from exactly the same clay, have so far withstood the action of the weather. In this case the material used was a very dense fine-grained one, but still permitted absorption.

Another means of preserving the glaze on the brick, is to burn them so hard that they do not absorb any water at all into the pores, and become completely vitrified like porcelain. Any other material, in which the ice needles are forced against the layer of glaze, and in which there is no internal room for expansion, will come to destruction sooner or later.

A brick which does not of itself withstand the action of frost, will in no way be protected from destruction by a layer of glaze on it, but it will be rather accelerated in this process of destruction, for the ice formed in freezing, can no longer escape freely from the pores, and comes against an impenetrable layer, which it gradually forces off together with adhering portions of the substance of the brick.

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### Examination of a Dull Black Roofing Tile Glaze

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PROF. EDWARD ORTON, JR., TRANSLATOR

The glaze under examination, which was used to color roofing tiles black, was distinguished by an intensely black-gray coloration, resembling graphite or roofing slate, but with only a very faint metallic gloss or luster. Since it adhered, compactly and without crazing, to a calcareous and buff-burning

clay, its fusibility must be low, for the tile remained porous in the firing which it received, and showed on its surface a pale sulphur-yellow coloration, but remained flesh-colored inside, as is characteristic of calcareous clays.

Under the microscope the glaze appears not as a perfect smooth glass, but as an uneven layer, which is formed by small crystalline segregations; the surface appears partly lowered and partly raised, by wart-like projections. On account of this structure, the property of refracting light or shining like a mirror is absent, and there remains only a faint metallic gloss.

An analysis of the glaze shows the following composition:

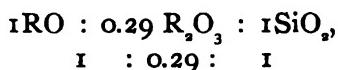
	Percent
Silicic acid	26.33
Alumina	5.43
Iron oxide	11.98
Manganese oxide	5.45
Lime	7.94
Magnesia	0.91
Lead oxide	39.78
Alkalies (by difference)	2.18
	<hr/> 100.00

A clean separation of the glaze from the body could not be accomplished by mechanical means, because the combination was such a close one that on chipping off a part of the glaze, a portion of the body always adhered with it. However, the glaze was soluble in cold dilute hydrochloric acid, and the body was only slightly attacked, so that a chemical separation was possible.

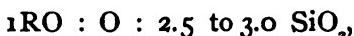
Splinters of the glaze, cracked off from the tiles which were sent for examination, were treated with dilute hydrochloric acid till the black shell was destroyed, and only a white skeleton of silica and lead chloride was left. The latter substances were dissolved out by treating the splinters with boiling sodium carbonate, and finally with dilute nitric acid.

As will be noted from the analysis, the glaze is extraordinarily rich in fluxes, and correspondingly poor in silicic acid. If the proportion of silicic acid to the sesquioxide bases be calculated, and also to that of the monoxides ( $RO$ —lime, magnesia,

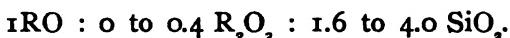
alkalies, lead, and manganese), the following proportion will be obtained :



while according to the researches of Benrath, the proportions in ordinary glasses amount to



and the proportions in the glazes in white ware and faience glazes according to analyses and published accounts in technical works and receipts, is calculated to be



The important quantities of the fluxes or basic elements, which occur in this case, appear to be the reason why this glaze lost, by crystalline segregations during cooling, its glossy luster, which, as has been proved by actual experiment, is just as characteristic of it when in the fused condition, as of all other glazes.

According to the researches of Ebell, made in the laboratory of the Braunschweig Polytechnic School, glasses in the fused condition are able to absorb a large quantity of metallic oxides and salts. Among the experiments which were made, iron oxide, manganese oxide, alumina, tin oxide, chromium oxide, and calcium oxide, were put into solution in glasses of ordinary crystal glass composition.

The results showed that when small quantities of these substances were dissolved, and the glasses were quickly cooled, they remained shining and clear, but that, when the quantities were increased and the cooling was made long-continued, they became completely dulled, and partly stone-like. On observing, with a low-power microscope, the splinters and chips which had been ground thin, it could be seen that the clear mass of glass was interlaced with fine crystalline needles, and could in most cases be proved to be the metallic oxides which had been added to the glass, and which had segregated out of them on slow cooling.

In the case in hand, we undoubtedly have to deal with such a glass, oversaturated with basic substances ; this is proved not

only by the analysis, where the bases strongly predominate over the acid or silica, but also by the crystalline character of the glaze under the microscope, and even with the naked eye.

The production of dull glazes as a means of decorating clay wares for architectural purposes (and the glazing of roofing tiles has to be regarded as a decoration rather than a means of protection) is often undertaken, but as the properties of glazes have been little understood, they have not been obtained by empiric processes with any certainty ; in most cases, the desired effect has been attained by making the glaze mixture so hard to fuse that it does not come to complete fusion during the firing.

The communication of this analysis, and of Ebell's results should be to many who desire to obtain dull glazes which shall be completely fused, a hint as to how to proceed to reach the desired result.

In order to make this analysis, which has been communicated, of practical value to those who are engaged in the manufacture of roofing tiles, the method of calculating a glaze composition from it, is imparted in the following paragraphs.

Every manufacturer will, for economic reasons, strive to use his own material as far as possible for his glazes, as far as its ingredients permit. For dark glazes one will as a rule be able to use impure brick clays, and it will be generally possible, as in the case before us, to compute the composition of the glaze ingredients, without slow and laborious empirical experiments, directly from the ingredients of the clay as known.

The brick clay serving as a foundation for the glaze corresponds in its extremes to the diluvial marl clays, which are so widely distributed, and of which we may take the Velten clay as a type. If this clay were taken as the basis of a glaze, the following calculation would be made :

Washed Velten clay has the following composition, as determined by Dr. Lindner in the laboratory of the Royal Porcelain Works :

	Per cent
Silicic acid	43.65
Alumina	12.09
Iron oxide	5.10
Lime	16.40
Magnesia	1.33
Alkalies	3.89
Loss on ignition	17.16

If the alumina content is to be taken wholly from the addition of the clay, then the quantity of this clay necessary to be taken is obtained from this proportion :

$$100 : 12.09 :: x : 5.43 \\ \therefore x = 44.90.$$

And, 44.90 parts of Velten clay contain, as fixed ingredients :

	Per cent
Silica	19.59
Alumina	5.43
Iron oxide	2.29
Lime	7.36
Magnesia	0.59
Alkalies	1.74

Deducting these figures from the figures of the glaze analysis, there remain the following substances to be added to the 44.90 parts of Velten clay in order to obtain a compound of the desired formula, namely :

	Parts
Silica	6.74
Iron oxide	9.69
Lime	0.58
Magnesia	0.38
Alkalies	0.44
Manganese oxide	5.45
Lead oxide	39.78

Silica and iron oxide can easily be secured as quartz sand and iron-red from the trade, and also lead oxide can be easily obtained. The addition of the small quantity of lime lacking is made by the use of calcium carbonate (chalk limestone). If one introduces in place of the ingredients which are regarded as unimportant (such as magnesia and the alkalies, but which are less easily added), an equivalent quantity of lime, a further addition of 0.79 part of

lime will be required. The total quantity of lime amounting to 1.37 parts will be equal to 2.45 parts of calcium carbonate. The manganese must be added as manganese dioxide or braunite. 5.45 parts of manganese oxide are equal to 6.69 parts of manganese dioxide, or 7.43 parts of 90 per cent braunite.

The composition expressed in round numbers will be as follows :

	Parts
Velten clay	45.0
Quartz sand	6.7
Iron oxide	9.7
Calcium carbonate	2.5
Litharge	40.0
Braunite (90 per cent)	7.5

from which one could expect a product perfectly equal to the original glaze.

A glaze compounded from the above formula, and burned at the temperature used in burning the marl clays (which is about or above the melting-point of silver), on a body of Velten clay, actually resulted in a glaze which, when burnt in an exclusively oxidizing atmosphere, was of a dark brown color, but on burning in a reducing atmosphere, gave a black-gray, with a metallic appearance entirely equal to the original glaze.

It will be an easy matter even for one without chemical knowledge to calculate for himself, after this example, the corresponding proportions from a chemical analysis under other conditions than those considered here, that is, when using another clay as a basis for the glaze.

### Note on Roofing Tile Glazes

PROF. EDWARD ORTON, JR., TRANSLATOR

The demands which are put forward by manufacturers of brick, in asking the assistance of chemists for obtaining suitable glazes, are generally such that cannot be met at all. They

finally ask for glaze receipts for easily fusible clays, the receipts being such which by their composition represent difficultly fusible glazes, like the slate-gray variety which is in such great demand.

Concerning the utility of roofing glazes, the following points must be brought out :

Roofing tiles should be glazed only when it is expected that they become by this treatment more able to resist the attacks of the weather, or if one expects or desires to decorate the ware and obtain certain ornamental effects not attainable by the clay alone. For this reason, dark glazes are required as a rule, as they are already adapted to roofing tile, which in most cases are made from dark burning clays.

No one should expect to use such glazes, unless he knows that his ware has the necessary degree of durability to carry them. It is known that soft-burned tiles, when they are exposed to the weather after glazing, generally shell off after a short space of time. Hence they are not improved by glazing. For this reason, it must be understood that tiles must be hard-burned if they are to be glazed, or at least medium hard, and it is better if they are vitrified, but under no circumstances should they be soft.

It is often the belief of brickmakers, who make tiles as well as brick, that they can burn their tiles soft because they keep their shape so much better, and that they can then glaze them and thus make them durable to weather. This is not the case by any means. If a roofing tile is soaked in water and is then frozen, one will be able to see that little rods of ice are forced out of every little hole or pore, and this effect is produced by the expansion which the water undergoes in freezing.

These little rods or needles of ice are the smaller in diameter the finer the grain of the clay, and the rods become coarser as the texture of the clay becomes more open. This can be noticed especially in washed limy clays; the ice flows through fine orifices, like a liquid; and if the orifices are closed up by a layer of glaze, and if the quantity of water contained in the tile is large, and the glaze does not adhere to the tile sufficiently, whole sections of the glaze will be burst off.

One will have to adjust the fusing-point of the glaze to suit the point of vitrification of the clay, for one always tries to burn body and glaze in one firing, where this is possible. The glazes by themselves will not always be capable of resisting the weather, especially the more easily fusible ones, but will be decomposed by the attacks of the air and water. Losses of alkaline matter occur in this way, and the structure of the glaze is by this means weakened, and becomes variegated, iridescent, and finally disintegrates into small floccules, when the whole glaze is destroyed.

Such glazes ought to be examined as glasses are, for in those, the action of the atmosphere is well considered. Weber has proposed a very good method for testing the resistance of glasses to the atmosphere, and this I have applied to glazes. The glazes are put under a glass bell-jar, under which a small dish of strong hydrochloric acid is also placed; this etches the surface more rapidly than the carbon dioxide of the air does, and in a short time, if the glass is destructible at all, it will show signs of decomposition, and a faint film of segregated silicic acid is seen on the surface.

The kind of a glaze which one would use for a roofing tile depends wholly on the temperature which the clay withstands. With a low heat resisting power one will always have recourse to the lead glazes, at least till a lead-free glaze is brought out, which will operate at these lowest temperatures.

The usual pottery glazes are simple lead silicates; they are the most easily fusible glazes, and are also employed in the manufacture of tiles. They vary in their silicic acid content from a sesquisilicate to a trisilicate, and contain a little alumina; the richer in silicic acid they are, the more difficultly fusible they will be. The compositions of the most easily fusible and the most difficultly fusible lead glazes are as follows:

Most easily fusible glaze	Most difficultly fusible glaze
1.0 X 223 lead oxide 1.5 X 60 silica	0.1 X 94 potash 0.2 X 56 lime 0.7 X 223 lead oxide 0.3 X 101 alumina 3.0 X 60 silica

The glazes applied must, as a rule, lie between these limits. One will of course always have to consider the degree of fusibility which can be permitted, and hence it will not only be possible, but necessary, to vary the numerical proportions considerably. In the glazing of tiles, where color is the chief requirement, and especially a black color, it will generally be best to use one's own clay as far as its composition will permit, and will use only lead oxide as an addition. The contents of iron oxide here act as a yellow or brown coloring material; other materials will generally be unnecessary for this purpose.

One must especially avoid boracic acid, because glazes calling for boracic acid must always be fritted, and this would not be advisable for a roofing tile glaze which has to be made as cheaply as possible. If colored glazes are desired, the color of the tile will first have to be obliterated, by a white layer, and a glaze containing tin oxide is best used for this purpose. The covering of the clay with a slip of white burning clay is not to be recommended.

The average composition of the white tin enamels, such as are used in the production of white tiles, faience, stove tiles, etc., can be taken as being

0.2 X 94 potash,  
0.8 X 223 lead oxide,  
0.2 X 101 alumina,  
2.0 X 60 silica,  
0.5 X 150 tin oxide.

Sometimes more of the one ingredient is necessary, and again more of another, but as a whole this will be the average composition.

The tin oxide makes the glaze opaque or white; any desired colors can be made with it by adding to it certain metallic oxides, for instance, cobalt oxide up to 3 per cent, copper oxide up to 4 per cent, manganese dioxide up to 8 per cent, iron oxide up to 4 per cent, uranium oxide up to 5 per cent, lead antimonate up to 10 per cent.

These lead glazes range, according to their composition, from about 500°, which is dark red heat, up to 1150°, the melting-

point of cone No. 1; above this heat, it is not possible to work lead glazes, as lead has the great disadvantage of volatilizing easily under the influence of the fire-gases. Through this peculiarity, the glaze grows constantly more acid, making it more difficultly fusible, and hence fails to come up bright.

This evil is made worse the longer the ware is kept in the fire, and it becomes the stronger the higher the heat at which the glaze is burned. Hence, in the composition of the lead glazes, one cannot very well exceed this limit; the tin glazes melt at about silver-melting heat, some above and some below, according to their constitution.

The most important glazes for roofing tiles are the glazes free from lead; these are used in the form of loam or loamy bodies, which are applied to the tiles, and burned on them. It is not possible to compound these loams in such a way that they will melt at any low temperature; they rather require a definite degree of heat to bring them to fusion at all. A glaze which has a composition, in equivalents, of



melts at about the temperature of cone No. 1. The lowest fusing-point which can be obtained for such glazes will be at about  $1150^\circ$ . They go up to cone No. 6 or 8, or even to cone No. 10.

These glazes, which must always contain iron, at least those which melt at the lower points of the scale, appear on fusing as a black layer, which takes on a brown coloration on the surface, if the glazes are exposed for a time to atmospheric air, like an ordinary stoneware glaze. If this glaze, free from lead, is heated for a time in a reducing atmosphere, the iron oxide will be reduced to the ferrous form, and the color will become black. In a similar manner a black coloration is induced if manganese is added to the glaze or copper oxide, cobalt oxide, etc., and it then remains permanently black, and does not turn to the yellowish brown coloration on a repetition of the oxidation.

The most important glazes used in the industry are the iron glazes, which, however, require more heat. They consist of ferrous silicates, corresponding to puddlers' cinder; they are

produced by saturating sand with iron oxide, generally impure ferruginous sand, or ochre blended with sand. The kinds of iron oxide or ochre, which are used for this purpose, always contain sand, and sometimes sand is even added. If the silicate is burned with exclusion of reducing gases, it assumes a brown coloration, but if burned in a reducing atmosphere, it will be pure black, and assume a slate-gray color on the surface. It does not melt completely to a thin fluid like the glasses, but really only frits together; the glazes never become bright and shining but are always dull. This is desirable, however, for roofing tile glazes.

The fusing-point of this glaze runs up to cone No. 10 or 11, and descends, depending on the composition and the ratio of silicic acid to the iron, to about cone No. 3. I have busied myself very much lately with glazes of this type, and have found that it is essentially the higher or lower per cent of silicic acid which determines the fusibility of a glaze.

The glazes richest in ferrous oxide are not always the easiest to fuse; the lowest fusing-point on the contrary lies near those which represent the bisilicate of iron (72 of iron, and 120 of silica). The fusibility decreases with a rising or a falling quantity of silica.

Glazes somewhat more easily fusible than the pure ferrous oxide glazes, are produced if a proportion of manganese oxide is added. Still no such glaze could be applied to a body which can not be burned at least to cone No. 3. Such glazes, which contain beside the ferrous bisilicate, other elements as well in considerable proportions, could be made more fusible than the ferrous glazes, but they would lose thereby the characteristic steel-gray luster, and turn into glassy, bright, black glazes. This rule is to be regarded as inflexible.

Glazes free from lead can not be burned at any heat below cone No. 1. Glazes containing lead must not be burned at temperatures above cone No. 1. This draws a sharp line between the two classes of glazes, which ought not to be overstepped.

Hence, if a chemist is asked to produce a formula for a glaze, which must be free from lead, and must be applied to a

body which cannot be heated above 1000° without danger, he will of course not be able to fill such a requirement.

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### Note on the Weather-Resisting Power of the Old Roman Bricks and Mortar

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ALBERT BLEININGER, B.S.C., TRANSLATOR

A piece of brick from the Roman baths of Trevres found its way into my hands. It showed a dense, gray, glaze-like coating on the surface about 1 mm. thick. This deposit appeared to indicate that a coating was applied in the burning of the brick and its presence was looked upon as the cause of the extraordinary weather resistance of the latter.

An examination, however, showed that the layer was by no means applied in the manufacture of the brick, but rather that it was produced by a deposition and incrustation of crystalline calcium carbonate in and on the brick, and that its existence is to be ascribed to the action of the mortar constituents acting for a long time.

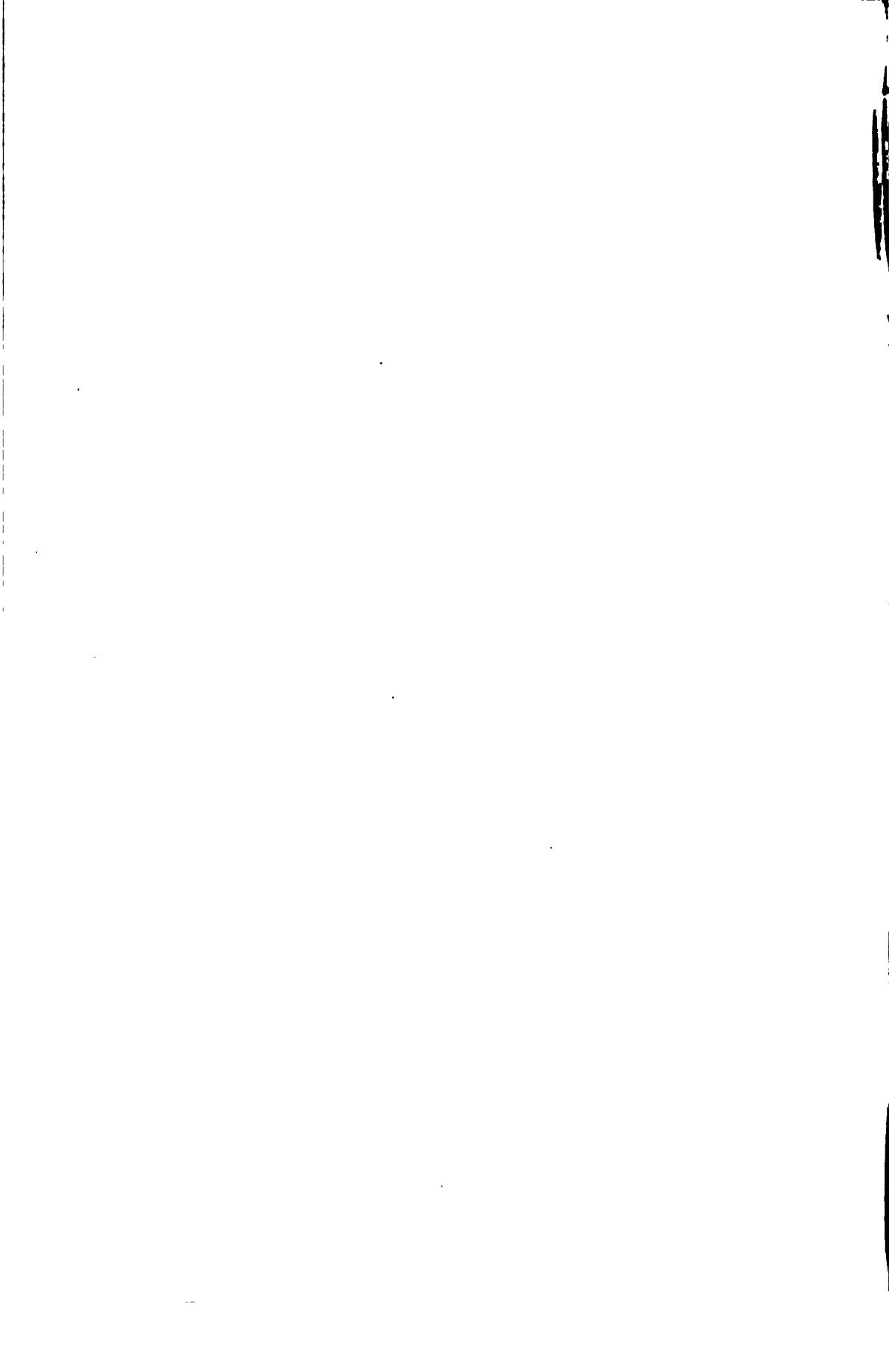
On touching the coating with hydrochloric acid, carbon dioxide was evolved energetically. The layer disappeared, and after a short time the brick assumed its original red color. Other places of the brick did not evolve any carbon dioxide with the exception of a few small white points on the fracture, which thus represented small particles of lime that had been burned "dead" in the burning of the brick, and hence did not affect its durability. The production of the limy coating on the surface is easily explained. Calcium carbonate, which is formed from the caustic lime of the mortar, is somewhat soluble in water containing carbon dioxide and on the expulsion of carbon dioxide it again crystallizes out. The carbon dioxide of the water has been taken from the atmospheric air. If the segregation takes place slowly the calcium carbonate may form crystals which are

visible to the naked eye, and hence give rise to the enamel-like appearance of the coating.

Otherwise, however, the bricks owe their durability (1) to the selection of a good clay, not too short, (2) to the uniform working of the same, (3) to the careful treatment of the brick during the making and drying, and (4) to the proper burning temperature and the thorough burning of the brick,—conditions which are self-evident for every good brick, but which to-day are not always given the necessary attention owing to the strong demand and the competition of modern times.

That calcium carbonate is easily crystallized from aqueous solution is proved by the crystalline structure of stalactites and stalagmites which are formed in limestone caves by the penetrating water, and is also observed in mortars. Thus, for example, there are found crystalline segregations in the mortar of the old Metz water works at Ars on the river Moselle in the shape of calc spar crystals grown in it, 2 to 3 mm. in size, which likewise can only have been produced by the long-continued action of water and carbon dioxide. The old mortars may in part owe their durability to such a change of the amorphous calcium carbonate to the crystalline, and future generations perhaps will express their surprise as to the excellence of our mortars, just as we do with reference to the Romans. The hardness of these mortars is solely to be ascribed to their age.

Later inquiries show that the surface of the brick which possessed the coating in question had been a contact surface, and was no doubt in contact with the mortar, offering a ready opportunity for the penetration of the lime into the interior of the brick. Another piece with an exterior surface showed only a blackish very thin deposit, which is to be considered as a deposition of dust and coal-like products.



## II. ESSAYS REFERRING TO EARTHENWARE AND STONEWARE

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### Tile Clay from Muehlenbeck

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ALBERT BLININGER, B.Sc., TRANSLATOR

The Velten stove-tile clay, which not only has given rise to an extensive manufacture of stove tiles at the village of Velten itself, but has also given rise to an export of raw and washed clay owing to its excellent quality, owes its special suitability for the manufacture of stove tiles essentially to two properties. The one property is the remarkably slight shrinkage which the clay shows in drying, and when burned soft, so that the stove tiles made from it do not warp in the kiln; the other property is that it carries a white tin enamel nicely and free from crazing. The last property is usually ascribed to its high content of calcium carbonate, which amounts to 25 or 30 per cent. Owing to the enormous consumption of clay (there being in Velten some 30 clay-working establishments which manufacture stove tiles), the time does not seem far distant when this valuable material will be exhausted and it will, perhaps, be of interest to become acquainted with other deposits which promise a similar material. The examination of such a material which is found near the deposit of the Velten clay, belonging to the same geological formation and showing similar properties, gave rise to the results of this investigation.

The clay is found at Muehlenbeck, a village north of Berlin, about 10 kilometers from Velten, and is being exploited in a newly constructed washing plant by Mr. T. H. Holzhueter in Licherfelde. It is the intention to sell part of it in the raw condition and to use part of it in the extensive manufacture of stove tiles, wall and floor tiles.

In the great deposit there are two clays of different color.

The deeper layers are blue-gray, and gradually change to a yellow clay towards the top. But evidently it is only one deposit which has thus been changed towards the top by the action of atmospheric influences and has assumed a yellow color. There are several places in the deposit in which white soft chalk is embedded in greater or smaller quantities. The material in the washed condition has the following composition :

	Yellow layer Per cent	Lower gray layer Per cent
Silica - - - -	42.31	41.03
Alumina - - - -	9.91	10.09
Iron oxide - - - -	4.88	4.20
Lime - - - -	19.95	20.99
Magnesia - - - -	1.86	2.14
Alkalies - - - -	1.66	1.64
Carbon dioxide - - - -	15.71	16.81
Water and organic matter - -	3.52	3.10
	100.00	100.00

The Velten clay is not always of the same composition. The content of calcium carbonate especially varies as is shown by two old analyses :

	Velten clay No. 1 Per cent	Velten clay No. 2 Per cent
Silica - - - -	47.86	43.48
Alumina - - - -	11.90	10.46
Iron oxide - - - -	5.18	5.10
Lime - - - -	14.96	18.68
Magnesia - - - -	1.71	1.42
Alkalies - - - -	3.66	4.00
Carbon dioxide - - - -	10.44 }	
Water - - - -	4.64 }	16.98

The content of calcium carbonate in these clays corresponds in No. 1 to 20.73, and in No. 2 to 33.4 per cent. In two other Velten clay samples, from different places, the content of calcium carbonate was found to be 27.4 and 28.9 per cent.

In the Muehlenbeck clays examined, the content of calcium carbonate was found to be 35.7 per cent in the yellow, and 38.2 per cent in the gray layer, this being still higher than the amount found in the Velten clay. The appearance of the clay from Velten and Muehlenbeck is the same. The latter forms a yellow or grayish mass of great plasticity; No. 1 especially is very plastic and exactly equal to the Velten clay, while the gray appears to be somewhat less plastic on account of its high content of lime; it readily assumes a yellow color on burning, and when heated to the melting-point of silver either shows no decrease in volume whatever or, on the contrary, a slight increase.

The shrinkages were measured and found to be as follows:

	Velten clay Per cent	Muehlenbeck clay	
		Yellow Per cent	Gray Per cent
On drying, starting with a condition of moistness corresponding to the working condition - - - - -		6.1	4.6
At the melting-point of silver - - - - -		6.0	4.6      3.4

The change in volume which the clay assumes in drying and burning is hence somewhat smaller than in the case of the Velten clay, and this property can influence the manufacture only in a favorable direction.

The washing, to which the clay has been subjected, is also favorable for its use. In the Velten clay there was found 39.08 per cent of fine quartz sand, while the sand content of the Muehlenbeck clay amounted only to 31.47 per cent in the yellow and 30.84 per cent in the gray variety. A practical test of glazing with a white enamel had a favorable result. The layer of enamel adhered perfectly to the surface of the Muehlenbeck clay and was perfectly free from crazing just as in the case of the Velten clay.

The clay from Muehlenbeck may for this reason replace the Velten clay, and owing to its good qualities will certainly find extensive use.

## Engobe Clays

(From Coeln-Meissen and from Kaschkau)

ALBERT BLEININGER, B.S.C., TRANSLATOR

Engobe clays are clays which on burning assume a pure white color, possess a certain degree of plasticity, and, when poured as a thin slip upon more or less colored clay wares, adhere to them in a thin coating and thus give to them a white color. After the burning, such clay wares are frequently coated with a colorless glaze. In central Germany and Bohemia this method is often used to give to stove tiles, wall tiles, and similar products a pure white color. White burning clays, which are adapted to this purpose, are rare, since there are but few plastic clays which burn to a pure white. The best known of these has so far been the Kaschkau engobe clay from near Meissen. It is obvious that in using such engobes the white clay as it is furnished by nature cannot be used without being washed and without the addition of certain constituents. The clays upon which the engobe is ordinarily applied when they are in the leather-hard condition, possess a varying composition at the different places of manufacture, and in consequence a different shrinkage, but the engobe can adhere to them only without cracking and shelling off when it possesses the same shrinkage as the working clay. The engobe clay offered by nature is a plastic clay which possesses a rather considerable shrinkage, and this must in most cases be decreased by an addition of a white burning, non-plastic substance, which shrinks little or not at all. As such additions there are used in different places white kaolin, quartz, feldspar, calc spar, and similar substances. The composition of the engobe body for a definite case cannot be given, without trial; it is always dependent upon the nature of the working clay and can be determined in any separate instance only by direct experiment.

The glaze to be applied is also dependent in its composition

upon the nature of the bulk clay. It can be said in general that the durability of the glaze is governed first of all by the durability of the working clay. The glaze is relieved from the defect of crazing only when the layer of engobe is very thick, or, as it is done in relief decoration, when the surface portions are molded with the white engobe mass, the usually coarser working clay being used to fill out the back. In this case the composition of the glaze must be so chosen that it unites firmly with the engobe clay. But where a thin engobe layer is used, which is applied by pouring, this will not be necessary, for on it the glaze will usually hold, independently of the composition of the engobe, if the working clay and the glaze agree in the contraction due to cooling.

It may be of interest to many to know that, beside the excellent Kaschkau engobe clays, there is a new material of this sort, mined and sold by Ruehle at Coelln, near Meissen. This engobe clay is a whitish gray, very plastic material, burning to a white, faintly cream color at a high temperature, but at a lower temperature or, as it will always be necessary, when mixed with other white burning materials, it burns to a pure white. Chemical analysis showed the following composition:

	Per cent
Silica	62.52
Alumina	25.57
Iron oxide	0.92
Lime	0.65
Magnesia	0.10
Potash	1.04
Loss on heating	<u>9.27</u>
	100.07

It is thus characterized as a plastic fire-clay, containing but little iron, of great bonding power and possessing a considerable content of quartz. In order to determine the amount of the latter a larger quantity of clay was first softened by soaking, and washed through a 900 mesh sieve. There remained a residue of coarser impurities (usually larger grains of pure quartz) of 3.8 per cent. The mass thus washed and purified was subjected to chemical analysis.

Another portion was unlocked with sulphuric acid (rational analysis), and showed the following composition:

	Per cent
Clay substance	72.05
Feldspathic residue	0.10
Quartz sand, not removed on washing	27.76

According to the trial burns made, the clay burns to a pure white at the temperature of the melting-point of silver ( $960^{\circ}$ ), but at a higher temperature, at the melting-point of gold, it assumes a slight yellowish tinge. This yellowish color may, however, be readily avoided by imparting a faint blue color to the glaze applied over the engobe.

The shrinkage of the clay from the wet, plastic condition, to that of complete dryness, amounted to only 6.9 per cent linear shrinkage; at the temperature of the melting-point of silver it shrank 1.9 per cent more; at gold, melting heat 2.5 per cent more, that is, not more than the shrinkage of lean working clays. According to the nature of the bulk clay it must be compounded in different ways for the purpose of engobing. Two different compositions of the engobe body were tested, a lean one (I) and a more plastic one (II).

## I

	Parts
Engobe clay from H. Ruehle	58
Meissen kaolin	45
Feldspar	35
Chalk	15
Ground quartz	60

## II

	Parts
Engobe clay from H. Ruehle	48.5
Ground marble	15.0
Ground quartz	36.5

Both engobes adhered well to a number of different clays and showed a very beautiful white color.

Let us now compare this clay with the old, famous Kaschkau engobe clay, which is mined on the estate of Mr. Ganssauge, at Kaschkau, near Meissen.

The clay existing there, which, as we are assured, still encloses an extensive area not yet opened up, is a light grayish material of a kaolin-like constitution, full of quartz grains up to the size of a pea.

On washing it 21.08 per cent of residue was held back by a sieve of 900 meshes per square centimeter. The fine, washed mass, on being analyzed by the rational method, showed the following composition :

	Per cent.
Clay substance - - - - -	67.82
Quartz sand - - - - -	30.93
Feldspathic residue - - - - -	1.25

The chemical analysis had the following result :

	Per cent
Silica - - - - -	63.17
Alumina - - - - -	25.09
Iron oxide - - - - -	0.64
Lime - - - - -	0.35
Magnesia - - - - -	0.26
Potash - - - - -	0.80
Water - - - - -	9.70

On comparing these figures of the rational and chemical analyses of the washed material with those of the first material, it will be found that they coincide as closely as it is possible for natural products to do. But there are a few small differences to which attention is to be called. First the content of iron oxide is still lower in the Kaschkau clay and hence it assumes a whiter color even at a high temperature. But I do not believe that the pure white color, as compared with the faint yellowish tinge of the Ruehle clay, will be of importance for many purposes. The faint cream color, which is noticed only when a pure white object is on hand for comparison, can easily be removed by a corresponding bluing of the engobe itself or of the glaze. Again, the glazes ordinarily applied on engobed bodies, which usually are high in lead, possess a more decided yellowish cast ; hence, most wares obtain their strong yellow color in this way. But where special stress is placed on a pure white color for finer ware and it is not desired to use a blue color in the en-

gobe and glaze, it will be necessary to make use of the pure white body.

However, an especially important feature of the old Kasch-kau body is its extremely small shrinkage in drying and burning within the temperature limits to which the burning of the engobe clays is usually confined. This is extraordinarily small and thus facilitates its adhesion to the main body.

The shrinkage in drying from the consistency necessary for the pressing of the washed engobe body in plaster molds amounted to 3.7 per cent; at gold-melting heat ( $1075^{\circ}$ ) it was equal to 4.1 per cent; at cone No. 1 ( $1150^{\circ}$ ) to 4.4 per cent. This is another well-founded reason why the old white engobe body enjoys such an excellent reputation.

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### The Fuerstenwalde Glaze Sand

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ALBERT BLEININGER, B.S.C., TRANSLATOR

The deposit of glaze sand at Fuerstenwalde belongs to the lignite formation and forms the cover as well as the intermediate layers of the lignite deposits opened up near the town; it is known to practical men as an easily fusible or "soft" sand and esteemed on account of these properties. Hence it often forms the raw material for the production of glazes, especially the lead-tin enamel used so extensively throughout northern Germany in the manufacture of stove tiles. In appearance it forms a very soft and flour-like, strongly dusting powder of a somewhat yellowish color, in which here and there small ochre-like particles, as well as particles of coal, are recognized. Numerous fine silver-white flakes of mica are also readily observed, especially on stirring it up with water.

The chemical analysis of the sand dried at  $120^{\circ}$ , resulted in the following composition:

	Total Per cent	Not decomposed by sulphuric acid Per cent	Clayey substance decomposed Per cent
Silica	85.96	80.03	5.93
Alumina	7.30	2.69	4.61
Iron oxide	2.22	—	2.22
Magnesia	0.25	—	—
Potash	1.97	1.00	1.14
Water and carbon- aceous matter	2.12	—	2.12
	99.82	83.80	16.02

In the residue remaining after decomposition by sulphuric acid, flakes of mica were observed more distinctly than in the raw sand. Assuming this mica to be potash mica (an assumption which is justified by the results of the analysis, and which consists of 48.07 per cent of silica, 38.41 per cent of alumina, 10.1 per cent of potash, and 3.4 per cent of water), then the content of alumina in the undecomposed part due to mica is calculated to be 7 per cent, and the mineral constitution of the sand would be expressed by the following composition :

	Per cent
Quartz powder	76.98
Mica	7.00
Clay substance	16.02

From this composition is explained its property of fritting at a comparatively low temperature with the fluxes (lead, tin oxide, and salt), and of thus producing a more fusible enamel than pure quartz sand ; for on the one hand it contains nearly one-fourth of its amount of such mineral substances which are relatively fusible in themselves without fluxes, and on the other hand it introduces into the glazes appreciable amounts of fluxes and hence furnishes, with otherwise the same composition, a glaze lower in silica but higher in alkali and alumina than pure quartz sand.

As may be seen from the above analysis, the sand contains an inconsiderable quantity of iron oxide, but as practice has shown, this has no essential influence upon the manufacture of enamels which contain all or part of the alkali in the

form of common salt, since the iron compounds are for the greatest part converted to iron chloride by the salt and are volatilized in fritting.

No less important than the chemical composition, in regard to the melting of the sand, is its physical constitution, the size and shape of its grains. In the following table are given the mechanical analysis of the same sand by means of the Schöne washing funnel, and also the physical analyses of two sands which are used in the Royal Porcelain Factory, one being a pure and moderately fine glass sand from Camenz, which serves for sanding the saggars, and the same sand, after being ground in the Alsing cylinder, is used for the porcelain glazes, in order to afford a comparison as to how far the Fuerstenwalde glass sand approaches the artificially prepared material for glazing in fineness.

	Glass sand from Camenz Per cent	Fuerstenwalde sand Per cent	Glass sand from Camenz, ground Per cent
Sizes of grain over 0.2 mm.	56.8	0.2	0.2
Sizes of grain from 0.02 to 0.04 mm.	43.2	57.5	29.9
Sizes of grain from 0.04 to .002 mm.	0.0	27.4	24.2
Sizes of grain from 0.02 to 0.01 mm.	0.0	6.4	3.2
Sizes of grain below 0.01 mm.	0.0	8.5	42.5

While most quartz sands consist of rounded grains, due to abrasion, the Fuerstenwalde glaze sand, like most of the lignite sands, shows an essentially different physical constitution, which certainly is of great influence upon its fusibility. On examining it with the assistance of a powerful magnifying glass or microscope, it will be observed that the predominating quantity of transparent quartz grains does not possess a round, but a plate-like, shape. Thus it offers a greater surface to the attack of the fluxes on melting than can be the case with sand consisting of round grains. Hence it is seen that the physical constitution of the material alone is of importance in regard to its fusibility.

## The Hoehr Stoneware Clay

ALBERT ELBINGER, B.Sc., TRANSLATOR

In the work of Dr. Wilkens ("Die Toepferei") in the discussion of the ordinary stoneware, the importance of a high content of silica in the clay is shown to affect the gloss and beauty of the salt glaze, and a number of analyses of stoneware bodies are given, these being made by Salrétat. These analyses show that the content of silica in the salt-glazed stoneware is always high and fluctuates between 62 and 75 per cent. The investigations, however, do not explain, from the chemical composition, the cause of the other characteristic properties of the clay, *i.e.*, of producing at a sufficiently high temperature a dense vitreous body, which absorbs no water and at the same time stands up well in the fire.

Of late the stoneware industry in the so-called "Nassau Kannenbaeckerland" has again received a powerful impetus. It produces not only the most ordinary pottery, but also in the hands of intelligent and active manufacturers, products of artistic value which enjoy a special reputation as decorative ware. I refer especially to products which are manufactured at Hoehr and Grenzhausen. Since the clay body used contributes much to the beauty of this fine, dense, pearl-gray pottery, it might interest not only those directly connected with the industry, but also wider circles, to learn something about the properties of the clay.

A chemical analysis of a sample of prepared clay, for which I am indebted to Mr. Hanke, of Hoehr, shows the following chemical composition :

	Per cent
Silica	70.12
Alumina	21.43
Iron oxide	0.77
Lime	0.00
Magnesia	0.39
Potash and soda	2.62
Water	4.92
	<hr/> 100.25

The rational analysis, whose importance in regard to the knowledge of clays has been shown in the investigation of porcelain clays, resulted in showing the following mineral constitution of the clay:

	Per cent.
Quartz powder	41.77
Unweathered feldspathic residue	3.50
Plastic clay substance	54.73

The percentage composition of the clay substance, proper, is as follows:

	Per cent.
Silica	47.45
Alumina	37.88
Iron oxide	1.41
Magnesia	0.71
Potash and soda	4.08
Water	9.00

On comparing these figures with those of the kaolin analyses, a similarity in composition is observed, the difference being only that in this case the content of alkaline fluxes is much greater and that of water lower. This composition explains, on the one hand, the ease of salt glazing, and on the other the peculiar density of the mass, owing to partial softening, not only of the feldspar present in small quantities, but also of the clay mass itself, which, on account of its high content of alumina, must show properties peculiar to the feldspar; this softening takes place far below the melting-point proper.

It is known that fusible silicates, like glass, glazes, and also clay bodies, do not change suddenly from the solid to the liquid condition; there appears a middle stage at which the mass is perfectly dense, its pores being closed, but the external shape, unless pressure is exerted upon it, will be changed little or only very gradually.

This peculiarity is true to a less extent of the silicious glasses and glazes low in alumina than of the substances high in alumina, as, for example, the feldspar. Who ever has had the opportunity of observing feldspar brought nearly to the fusing-point, will be able to recognize a similarity between it and completely vitrified clay. If feldspar powder or feldspar is molded together with different amounts of fire-clay into small pyramid-like bodies

which are burned, it may be observed that they are sometimes glassy at the fracture and become strongly translucent without having in the least lost the sharpness of the edges. This property of viscous fusion of the fluxes appears to be related to their content of alumina; at least other fluxes containing lime or alkali, show this property in a less degree, and change directly from the solid condition to the thin liquid state with but a slight rise in temperature.

### Volcanic Sand from the Eifel Mountains

ALBERT BLEININGER, B.Sc., TRANSLATOR

The sand represents a dark gray sharp powder, which, in part owing to subsequent infiltration of cementing substances, forms larger lumps easily crushed by the hand, and in part black pieces showing a crystalline fracture. On heating, it first loses a small quantity of water, assumes a light reddish brown color owing to the oxidation of the black ferrous oxide contained in it to ferric oxide and fuses at about 1200° to a blackish-brown glass.

The chemical composition of the sands was found to be :

		Coarse sand. Per cent.	Fine sand. Per cent.
Silica -	- - - -	52.61	52.31
Alumina -	- - - -	13.98	15.75
Ferrous oxide -	- - - -	8.49	7.22
Lime -	- - - -	10.92	10.47
Magnesia -	- - - -	7.81	7.04
Potash -	- - - -	1.69	2.26
Soda -	- - - -	2.36	3.10
Phosphoric acid -	- - - -	trace	trace
Sulphuric acid -	- - - -	0.52	0.38
Loss on heating -	- - - -	1.57	1.43
		99.95	99.96

The composition of the sands, hence, is nearly the same. According to analysis the sands are entirely excluded from being used in the manufacture of fire-brick. The quantities of flux, ferrous oxide, lime, magnesia, potash, and soda are much too large.

However the material could be used when added to refractory clays in the shape of a fine powder, for the manufacture of floor tiles, or it may be used as a glaze material for refractory clays.

The sand could likewise be used for less refractory clays in the manufacture of such products for which the brown color of the glaze either does no harm or is even desirable. Thus it could be used for some kinds of ordinary pottery, for glazed bricks, water pipes, roofing tile, and similar products. Finally the sand might find application in the manufacture of ordinary colored glass, wine and beer bottles; for this purpose it would need only an addition of lime and sand.

### Braunite from Luthersteufe

ALBERT BLAENINGER, B.Sc., TRANSLATOR

The material existing in great deposits is mined near Ilmenau, and is offered to the market in the following grades:

	I Per cent	II Per cent	III Per cent	Braunite dust Per cent	Washed dust Per cent
Gangue and silica	4.77	1.90	9.19	11.67	10.41
Alumina	0.64	0.44	1.49	0.24	0.52
Oxide of iron	0.14	0.12	0.49	0.97	1.26
Lime	0.91	0.56	0.43	0.15	0.05
Barium oxide	0.43	—	0.10	0.25	0.27
Copper oxide	0.21	0.21	0.19	0.08	0.15
Nickel and cobalt oxide	—	—	—	0.80	0.58
Oxygen	15.41	9.47	7.24	10.88	11.11
Manganous oxide	74.26	84.98	74.76	66.97	71.02
Water and loss on ignition	3.23	2.32	6.11	7.99	4.63
	100.00	100.00	100.00	100.00	100.00

If the oxygen contained in the braunite is calculated to be combined with the manganous in such a manner that manganese dioxide is produced, the braunites will contain the following amounts of dioxide:

	I Per cent	II Per cent	III Per cent	Dust Per cent	Washed dust Per cent
Dioxide - -	83.64	51.52	39.34	49.50	51.11
Manganous oxide - -	6.03	42.93	42.66	17.02	31.02

The braunite is especially valuable because iron oxide is almost entirely lacking as well as calcium carbonate, thus allowing the production of a purer color. The material is particularly valuable for the glass industry, since on decolorizing the glass no disturbing effects are produced, and only a slight quantity is necessary for this purpose.

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### Notes on the Composition of Brown Slip Glazes

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ALBERT BLEININGER, B.S.C., TRANSLATOR

The stoneware industry in many districts makes extensive use of very fusible clays for producing on fire-clays extremely durable glazes, free from poisonous metals. In part these are materials of an ochre-like or marly character, and are partly ferruginous clays, which are freed from coarse impurities and sand, if necessary, by washing and sieving, and are applied on the objects to be glazed, which are in the semi-dry condition, by dipping, pouring or brushing. The so-called "Bunzlau pottery" which is manufactured in many districts of middle Germany, in the Lausitz, in the kingdom and in the province of Saxony, and in Bohemia, is an excellent type of this class of ware, using a very beautiful yellowish brown slip glaze which is extremely durable, and is applied as de-

scribed above. Such slip glazes are used extensively also in the glazing of water and sewer pipe, for agricultural purposes and chemical factories, and to a slight extent also for architectural ornaments. The use of clay glazes always presupposes the use of a rather refractory clay for a body, since the temperature required for melting the glazes (beginning or complete white heat) is much higher than that for lead glazes.

The materials suited for the glaze are by no means rare, and a great number of brick clays are used either directly or compounded with cheap fluxes. For this purpose there are added to the washed glaze, calcareous materials, chalk, marl, or solutions of potash, soda or salt; or again the fusion of the glaze is promoted at the end of the burn by throwing salt into the kiln or furnace, as is being practiced in the manufacture of pipes.

But not always will such additions suffice to produce a suitable glaze, for though they lower the melting-point they at the same time change the color to an undesirable extent, and the intended pleasant yellowish brown glaze is changed to one that is translucent or transparent dark gray to yellowish green, which crazes easily.

The clays used for brown glazes contain both iron and lime; at a low heat they assume a red color which continues to become darker brown or blackish brown with increasing temperatures. On softening they first form an opaque black, later on a blackish green, translucent, obsidian-like glass, which, on cooling in an atmosphere containing oxygen, is coated with a faint yellowish brown to bright red skin, very probably segregated oxide of iron.

The fusibility of the slip glazes, as of glasses and glazes in general, is dependent on the proportion of fluxes (lime, magnesia, alkalies, oxide of iron) to silica and alumina; the color is a function of the iron content and perhaps also of the ratio between it and the other fluxes, since it is known that on adding fluxes to the glaze the latter loses its property of becoming coated with the brown surface color so desired on cooling and also changes to an opaque black or translucent green glass.

In order to collect some information in regard to the composition of these glazes, three of these washed clays, often used for this purpose, were analyzed:

First, the slip clay from Naumburg, which is often used in the Lausitz, and especially at Bunzlau for the manufacture of the well-known brown cooking ware and sewer pipe;

Second, the slip clay from Camenz, likewise used for brown cooking ware;

Third, a glaze from the sewer-pipe works at Dommitzsch.

The chemical analyses of these slip clays gave the following compositions:

Glaze from	Naumburg Per cent	Camenz Per cent	Dommitzsch Per cent
Silica - - -	58.99	64.49	62.40
Alumina - - -	11.73	14.35	15.51
Oxide of iron - - -	4.16	4.38	5.68
Lime - - - -	7.47	4.13	4.86
Magnesia - - -	1.83	1.53	1.13
Alkalies - - -	4.83	3.69	3.62
Carbon dioxide - -	6.19	3.12	2.88
Chemically combined water and organic substance }	4.80	4.31	4.41

The examination in regard to the mineral constituents of the slip clay, by means of the so-called rational analysis, which is so important for the knowledge and consideration of clayey materials, gave the following compositions:

Glaze from	Naumburg Per cent	Camenz Per cent	Dommitzsch Per cent
Fine quartz sand -	38.89	34.34	29.27
Feldspathic residue -	17.79	13.72	15.98
Plastic clay substance -	29.25	44.85	48.21
Calcium carbonate -	14.07	7.09	6.54

In order to compare the relative fusibilities of the glazes with each other, these three kinds of glaze slip were applied to

the outer surface of a small hollow cylinder, 6 cm. high and 4 cm. in diameter, the exterior surface being divided into three equal areas; the glaze was applied by means of a brush. In the interior of the cylinder there were placed three tetrahedra formed from the same materials, 3 cm. high, and with an edge of 1<sup>cm.</sup> at the base. For comparison a like pyramid of powdered Norwegian feldspar was placed in it, the whole being heated on a small plate of refractory clay in a fire-clay saggar to the melting-point of pure gold, that is, about 1200°. In this test the Naumburg glaze proved to be by far the most fusible one; this glaze had become a thin liquid, transparent, very glossy, greenish brown in color and had run off at the lower edge of the trial piece. The pyramid trial had spread upon the plate as a blackish green, dense glass, nearly free from bubbles. The next in fusibility was the glaze from Camenz; this glaze was olive-brown, not transparent but very glossy, and had by no means run off; finally the glaze from Dommitzsch was opaque, blackish brown with but little gloss and showing on the surface the streaks caused by the application with a brush. The pyramid trials of the last two were found to be blackish brown, shapeless masses of slag, full of large blisters. The feldspar showed only indications of fusion; the pyramid formed from it had shrunk, but retained its sharp edges perfectly and had become a dense translucent porcelain-like mass with a slight exterior gloss.

Seeking for a numerical expression of the fusibilities from the results of the gross analyses, according to the principles which I have laid down,<sup>1</sup> a result is obtained which coincides very closely with the practical experiment. This principle is permissible in this case since here, unlike in clay, all the constituents really are transformed to a single glass-like compound.

Calculating the proportion of the fluxes (RO) to the alumina and silica the following values are obtained:

<sup>1</sup> See Seger: "Ueber den Einfluss der naheren Bestandteile des Thones auf die Schmelzbarkeit." Thonindustrie Zeitung, 1, 296 (1877).

	Refractory quotient (Seger)
Glaze from Naumburg	$RO : 0.40 Al_2O_3 : 2.30 SiO_2 = 0.47$
Glaze from Camenz	$RO : 0.68 Al_2O_3 : 3.53 SiO_2 = 0.81$
Glaze from Dommitzsch	$RO : 0.80 Al_2O_3 : 3.15 SiO_2 = 0.86$
Glaze from Feldspar	$RO : 1.01 Al_2O_3 : 3.86 SiO_2 = 1.26$

It is seen that the figures theoretically deduced, coincide throughout with the practical test, and that the smaller values actually correspond to a greater fusibility.

According to the method of calculation of Bischof the numerical values would be:

	Refractory quotient (Bischof)
Glaze from Naumburg	2.30
Glaze from Camenz	3.53
Glaze from Dommitzsch	3.15
Glaze from Feldspar	3.86

which do not agree with the practical test.

### Note on Glazes Free from Lead

ALBERT BLEININGER, B.Sc., TRANSLATOR

It is a well-known fact that the white ware and the earthenware industries, as well as allied branches, have used up to the present time exclusively such glazes which contain lead oxide

The Norwegian feldspar used, from the Royal Porcelain Factory at Charlottenburg, had the following composition:

	Per cent.
Silica	64.98
Alumina	19.18
Iron oxide	0.33
Magnesia	0.25
Potash	12.79
Soda	2.32
Loss on heating	0.48
	<u>100.33</u>

From this there is calculated the formula



as the only or partial flux, while our porcelain industry employs glazes which contain as fluxes only the alkaline earths, alkalies and alumina, and thus are free from lead.

Protests have repeatedly been raised against the use of lead glazes. It has been pointed out that the lead glazes of the potters, which are simply made by fusing a mixture of lead oxide, sand or clay on the surface of the ware, easily lose their lead oxide to fatty or acid liquids, and, owing to the poisonous property of the lead, could do injury to the health of the public. This is, however, not always the case, but applies essentially only to common earthenware and partly to white ware, for which the glazes are, as a rule, first fritted in order to render the lead oxide more stable. This danger could be removed in many cases by careful preparation of the glaze and hard burning. There always remains, nevertheless, some danger for the workmen who manipulate lead glazes. The operatives who apply and brush off the glazes breathe the dust containing the lead, take it up in their clothes, and have it deposited on their skin. In larger factories suitable provisions for cleaning, ventilating, and washing are made, and are very beneficial, but frequently in smaller establishments all precautions are entirely disregarded or are difficult to introduce.

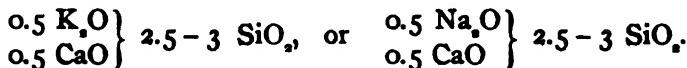
I have now been engaged for many years in trying to do away with the poisonous lead oxide as a glaze material as much as possible, and have endeavored to bring the question nearer solution by suggesting the use of barium in glazes in place of lead. I have made practical propositions for the use of such glazes, have used such glazes in my own work and have agitated their use publicly.

I do not deny that the production of barium glazes which for practical purposes can be made only with heavy spar is more or less difficult for the manufacturer who is not a chemist, and failures may result. For this reason I have attempted the solution of this problem in another way, and have followed the porcelain glazes, glazes high in alumina which as fluxes contain alkalies and lime, whose fusibility is increased by the partial substitution of silica by boric acid. It is thus seen that with

the exception of the lead oxide there are present practically the same substances which in greater or smaller quantities make up the ordinary glazes. In my experiments, however, the main consideration was the maximum and minimum amount of the substances admissible in the glazes in order to produce good, smooth, and transparent coatings of glass on the body at the temperature of the ordinary white ware glost-burn. The lead oxide without doubt is the metallic oxide most suited for the production of glazes. Its insolubility in water which permits of its use in the free condition, the instability of its compounds, especially of the carbonates and sulphates, its fusibility and the fusibility of its silicates, the variety of proportions in which it can enter into glazes, producing nearly always clear glazes, the gloss and high index of refraction as well as the beauty of the colored lead glasses, are properties which no other metallic oxide can attain; these are all reasons why lead oxide is so suitable as a glaze material. The only fault it possesses is the poisonous character of its compounds which endangers the consumer as well as the workman. If I now make the attempt to replace lead glazes by lime-alumina glazes, I do not assert that this can always be done. The lead glazes will still be necessary in all the branches in which the pottery requires an artistic treatment. However, the substitution will be possible in the glazing of white ware, also of ordinary earthenware, that is, for plain colored or light white ware, as well as that decorated with underglaze colors of the most various kinds. At this point I wish to call attention to the fact that the pottery coated with a glaze free from lead assumes a different character entirely; it loses the gloss peculiar to lead glazes and assumes more the character of the porcelain glazes. In how far this may injure or benefit the industry commercially, I shall not venture to say. But I believe that this question will not offer an obstacle to the use of glazes free from lead.

Oxide of lead as such, litharge or carbonate of lead (white lead), can always be added to a glaze mixture, without injury, since it itself becomes liquid, always fusing readily to a clear glass which covers the body or shows the color applied under the

glaze. The case is essentially different with the lime glasses. The lime is infusible by itself, and hence is dissolved by the glaze more difficultly. Hence in order to obtain solution, lime must be added to the glaze materials in small quantities and in a state of finest subdivision. Again, lead oxide may be the sole flux of a glaze, at least other materials are not necessary in order to form a glaze, but we know from the glass industry that lime glasses are transparent only when they contain also alkalies as fluxes. The composition of a normal glass is always assumed to be as follows:



Similar proportions must be assumed for glazes. It would not be permissible to fuse the alkali alone with the silica as a frit and then to add the lime, because the alkali silicates produced would be dissolved in the water on grinding and would thus be taken from the glaze. It would be difficult to give to the glaze a definite composition in this way. The higher the frits are in lime, the more insoluble will they be in water on grinding and the less the danger of loss of alkali in the grinding of the frit.

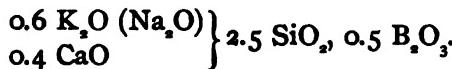
Referring to the experiments described in the following:

I wish to state that I have used as alkali, at one time potash and again soda, and that I have found, beside a slightly greater fusibility of the soda glasses, no difference in the behavior of the glazes. However, I have ordinarily used both together which, as experience has shown, gives rise to a still greater fusibility than when only one of the alkalies is used. I have also considered only such glazes which demand a finishing temperature below the melting-point of gold, because this is the highest heat which is required for ordinary earthenware and white ware glazes.

I have proceeded in my experiments quite systematically, and have first worked with the highest content of alkali which may be attained without an appreciable solution of the frits on grinding and have increased the other constituents, alumina, silica and boric acid, in varying proportions. Then I have

lowered the alkali content of the glazes but have increased the proportion of lime and observed how the glazes were affected by this change as well as by changing the fixed constituents, alumina and silica.

I. Glazes and frits of the composition



Three frits were used for the production of this series:

1. A lime frit made from

	Parts
0.6 equivalent potassium nitrate - - -	60.60
0.4 equivalent calcium carbonate (marble) - - -	20.00
2.5 equivalents ground quartz sand - - -	75.00
0.5 equivalent boric acid, hydrous - - -	<u>31.00</u>
	186.00

After the expulsion of water and carbon dioxide, there remained of this frit 131.9 parts by weight.

2. A potash-soda frit made from

0.3 equivalent potassium nitrate - - -	30.30
0.25 equivalent borax - - -	47.75
0.05 equivalent enameling soda - - -	2.65
0.40 equivalent marble - - -	20.00
2.50 equivalents ground quartz - - -	<u>75.00</u>
	175.70

of which 127.10 parts remain after ignition.

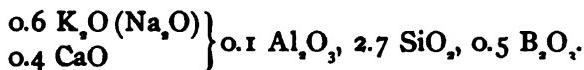
3. A soda frit made from

0.6 equivalent enameling soda - - -	31.80
0.4 equivalent marble - - -	20.00
2.5 equivalent ground quartz - - -	75.00
0.5 equivalents boric acid, hydrous - - -	<u>31.00</u>
	157.80

of which 122.30 parts remain after ignition.

All these frits showed a similar behavior since they have a similar composition except for the fluctuations in the proportions of soda and potash. They fused at a temperature below the fusing-point of pure silver, and became clear colorless glasses at a temperature a little above the melting-point of gold. These were ground, according to their equivalent proportions (131.9, 127.1 and 122.3), with one-tenth of an equivalent of pure clay

substance, 12.95 parts (Zettlitz kaolin), so that a glaze was formed of the composition



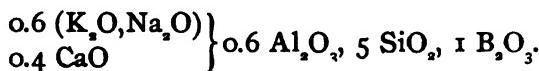
This glaze melted at from silver melting heat up to the temperature of fusion of an alloy, 80 parts silver and 20 parts gold, to a clear and smooth coating of glaze, and was found to be less injurious to underglaze colors than most lead glazes. The glaze adhered only to a hard-burned body, very high in quartz (35 clay substance, 5 feldspar, 60 quartz, burned between cone No. 9 and 10). On a body higher in clay or burned softer the glaze crazed immediately or after a few days. When the addition of kaolin to the frit was increased and in place of 0.1 equivalent, 0.2 = 25.9 parts of Zettlitz kaolin was used, perfectly bright and glossy glazes were still produced on rapid cooling; on very slow cooling, in a tightly luted muffle, however, the glaze was at times slightly dimmed; this dimming was much more pronounced on a further increase of the clay substance to 0.3 equivalent, or 38.85 parts. The glaze assumed an opalescent appearance and hence became unsuitable as a glaze. The crazing was decreased by the addition of clay as I have shown on a previous occasion. The same was true when in the second of the glazes used the silica content was increased.

In this series the content of silica could be increased to 3.5 equivalents; that is, beside 0.2 equivalent = 25.9 parts of Zettlitz kaolin, 0.6 equivalent = 18 parts of quartz, could be added without injuring the glaze. This proportion of alkali to lime, and this content of alumina and silica must not be exceeded; for on the one hand the melting-point is thus raised and reaches the allowable maximum in this composition, and on the other hand glazes, containing much quartz not fritted in, do not dissolve the latter and do not fuse to a clear glass, but the quartz floats as a thin coating on the surface.

If the content of alumina and silica is increased still more with a simultaneous increase of boracic acid, the fritting must be carried much higher in order to dissolve the clay introduced.

But this always produces more or less opaque glasses while, as we will see later, with a low content of alkali and high proportion of lime, the introduction of much alumina leads to the production of clear and beautiful glasses.

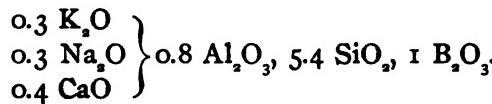
A glass of the composition



produced from

	Parts.
0.30 equivalent potassium nitrate - - -	30.30
0.25 equivalent borax - - -	47.75
0.50 equivalent enameling soda - - -	2.65
0.40 equivalent marble - - -	20.00
0.60 equivalent Zettlitz kaolin - - -	77.70
3.8 equivalents quartz sand - - -	114.00

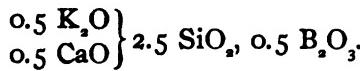
and fused to 245.35 parts, on rapid cooling becomes slightly opalescent, on slow cooling, however perfectly white and opaque. But this opacity disappears as soon as the alumina content is raised still higher by an addition of Zettlitz kaolin. An addition of 0.2 equivalent, that is, 25.9 parts of Zettlitz kaolin to 245.35 parts of frit, about 10 per cent of kaolin, produced a beautiful glaze answering all requirements, having the composition



II. Glazes and frits with the alkali-lime proportion 0.5 K<sub>2</sub>O, Na<sub>2</sub>O, 0.5 CaO, and the same silica and boric acid content as before.

These glasses behaved essentially like the preceding series; in this series glazes were made containing potash or soda or both. For making the glazes, frits of the following composition were fused:

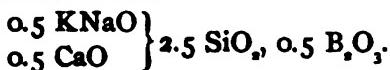
#### I. Potash-lime frit



	Parts
0.5 equivalent potassium nitrate - - -	50.50
0.5 equivalent marble - - -	25.00
2.5 equivalents quartz sand - - -	75.00
0.5 equivalent hydrous boric acid - - -	31.00
	<hr/> 181.50

or after fusion 130 parts.

2. Potash-soda-lime frit



0.25 equivalent potassium nitrate - - -	25.25
0.25 equivalent borax - - -	47.75
0.50 equivalent marble - - -	25.00
2.50 equivalents quartz sand - - -	75.00
	<hr/> 173.00

or after fusion 126 parts.

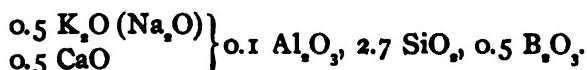
3. Soda-lime frit,



0.25 equivalent enameling soda - - -	21.20
0.25 equivalent borax - - -	47.75
0.50 equivalent marble - - -	25.00
2.50 equivalents quartz sand - - -	75.00
	<hr/> 168.95

or after fusion 122 parts.

On grinding these frits together with 0.1 equivalent of Zettlitz kaolin according to the equivalent amounts of 130, 126, and 122 parts, 0.1 equivalent of the kaolin being 0.1 ( $\text{Al}_2\text{O}_3, 2\text{SiO}_3 + 2\text{H}_2\text{O}$ ) = 12.95 parts, there is produced a glaze of the composition



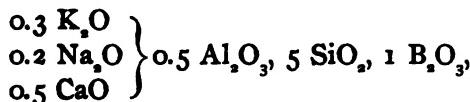
This glaze likewise produces a perfectly clear and good coating at a temperature of 20 gold, 80 silver to 50 gold, 50 silver, but this glaze, like the preceding ones, adheres only on a body very high in quartz.

On increasing the content of clay substance, taking for 1 equivalent of frit (130, 126, or 122 parts) 0.2 equivalent or 25.9

parts of clay, the mixture will also produce a good glaze if burned rapidly, and especially if cooled rapidly; when cooled slowly it becomes milky.

With a still greater addition of clay, 0.3 equivalent = 38.8 parts and more, the glaze becomes very cloudy. The mixtures containing much alumina, and at the same time possessing a higher content of boric acid, also behaved practically like the corresponding glazes of the preceding series with a still higher content of alkali. They were melted at a high heat (cone 8 to 10) in order to bring the clay in solution during the thin-liquid state. After fusion and cooling they were ground and without further addition applied as glazes.

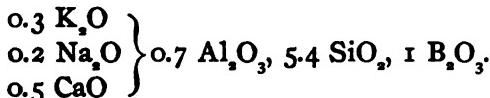
There was fused a glaze of the composition



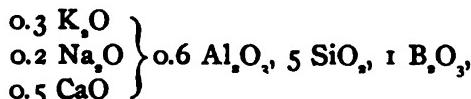
from

	Parts.
0.3 equivalent feldspar	83.55
0.2 equivalent borax	38.20
0.5 equivalent marble	25.00
0.2 equivalent Zettlitz kaolin	25.90
2.8 equivalents quartz sand	84.00
0.6 equivalent hydrous boric acid	37.20

This glaze melted to a clear glass, but became dim on slow cooling; on the body it fused to a milky coating. However, when a still further addition of Zettlitz kaolin was taken and ground together with it in the mill, in the ratio of 90 : 10, there was produced at about gold-melting heat a transparent layer of glaze which did not craze even on a body high in alumina (50 per cent clay substance, 5 per cent feldspar, 45 per cent quartz) which had been burned softer. The chemical formula of the glaze is



Similarly a glaze containing a still higher content of alumina, incorporated by fusion, of the composition,



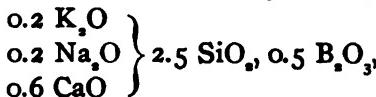
and compounded from

	Parts
0.3 equivalent feldspar	83.55
0.2 equivalent borax	38.20
0.5 equivalent marble	25.00
0.3 equivalent Zettlitz kaolin	38.85
2.6 equivalents quartz sand	78.00
0.6 equivalent hydrous boric acid	37.20

adhered well on a soft body high in alumina, and even on slow cooling formed a perfectly clear glaze.

III. Glasses with the alkali-lime ratio of 0.4 ( $\text{K}_2\text{O}$ ,  $\text{Na}_2\text{O}$ ): 0.6  $\text{CaO}$  and a silica-alumina ratio as before.

First a frit was fused of the composition,



consisting of

0.2 equivalent potassium nitrate	-	-	20.2
0.2 equivalent enameling soda	-	-	10.6
0.6 equivalent marble	-	-	30.0
2.5 equivalents quartz sand	-	-	75.0
0.5 equivalent hydrous boric acid	-	-	31.0
			<hr/> 166.8

being 124.9 parts after fusion.

The mass was very milky and dimmed after fusion and slow cooling, especially on the walls of the crucible, while it formed a clear glass in the interior.

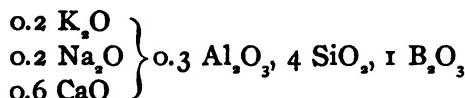
Ground together with 0.1 equivalent of Zettlitz kaolin (124.9 : 12.95) the glass produced a milky coating of glaze and was hence unsuitable as a glaze. It was now tried to remove the milky dimness of the glaze by increasing the content of boric acid. Against all expectations it was found that on increasing the content of boric acid the dimming became more and more pronounced. In other instances, to be described later, this also took place.

When a frit, like the preceding one, was melted with the

double amount of boric acid a much more intensely dimmed glass mass was obtained.

For this reason further attempts to produce glazes with frits free from alumina or low in it, were not made, and only frits with a high content of alumina were employed because these proved more successful.

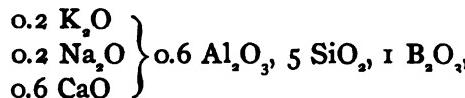
A glaze of the composition



was found to become dim.

The cause of the dimming was here a too low alumina content, for the trouble disappeared on increasing the alumina.

The glaze became clear and stable with a composition of



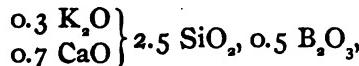
The melting-point of this glaze lies somewhat below gold-melting heat; it was composed of

0.2 equivalent potassium nitrate	-	-	20.2
0.2 equivalent crystallized borax	-	-	38.2
0.6 equivalent marble	-	-	30.0
0.4 equivalent Zettlitz kaolin	-	-	51.8
4.2 equivalents quartz sand	-	-	126.0
0.6 equivalent hydrous boric acid	-	-	37.2

Glazes still higher in alumina, on fusing together the above frit with 10 per cent of Zettlitz kaolin, were likewise satisfactory and suitable for technical purposes.

#### IV. Glasses with an alkali-lime ratio of 0.3 K<sub>2</sub>O : 0.7 CaO and an alumina and silica content as before.

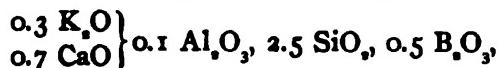
The glasses free from alumina, of the composition



were compounded and fused like the preceding ones, but produced perfectly milky masses, entirely unsuitable as glaze frits. Similarly, mixtures with a low content of clay were perfectly opaque.

They became clear only when the addition of clay was considerable.

There was melted a glass of the composition

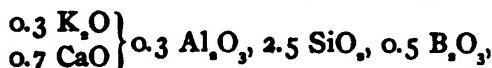


from the following constituents :

	Parts.
0.1 equivalent feldspar	27.85
0.2 equivalent potassium nitrate	20.20
0.7 equivalent marble	35.00
1.9 equivalents quartz sand	57.00
0.5 equivalent hydrous boric acid	31.00

The glass thus obtained was white and perfectly opaque, even on rapid cooling.

Another glass was fused having the composition

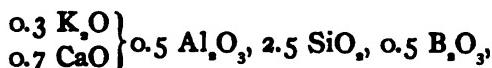


from the following constituents :

0.3 equivalent feldspar	83.55
0.7 equivalent marble	35.00
0.7 equivalent quartz sand	21.00
0.5 equivalent hydrous boric acid	31.00

The glass fused to a clear and transparent mass, but after cooling became more or less opaque.

Still another glass was melted,



from

0.3 equivalent feldspar	83.55
0.2 equivalent Zettlitz kaolin	25.90
0.7 equivalent marble	35.00
0.3 equivalent quartz sand	9.00
0.5 equivalent hydrous boric acid	31.00

The slight dimming of the glass now disappeared ; there was obtained a glass which remained perfectly clear on slow cooling and also after grinding produced a clear glaze on the body, but it was found that it was not suitable as a glaze after all. The glass being applied in the ground condition, there

always appeared on top of the glaze a transparent, wrinkled coating which robbed the glaze of its gloss. This fault disappeared more and more with an increasing content of acid. The content of acid in the subsequent experiments was fixed at 3 equivalents silica, 1 equivalent boric acid, 4 equivalents silica, and 1 equivalent boric acid, 5 equivalents silica, and 1 equivalent boric acid, maintaining the old relation of the alkalies, lime and alumina. In the last two compositions the wrinkled skin on top of the glaze disappeared completely. In next to the last, however, a slight, in the last a distinct, opalescence of the glass was shown. This disappeared entirely on increasing the alumina content of the glaze still more by grinding 10 per cent of Zettlitz kaolin together with the frit and applying this mixture. The varying amounts of boric acid likewise exert a considerable influence upon the transparency of the glass.

There were melted three frits :

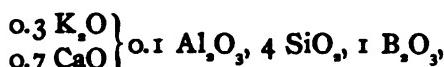
1.  $\frac{0.3 \text{ K}_2\text{O}}{0.7 \text{ CaO}} \left. \begin{array}{l} \\ \end{array} \right\} 0.5 \text{ Al}_2\text{O}_3, 4 \text{ SiO}_2, 0.5 \text{ B}_2\text{O}_3$
2.  $\frac{0.3 \text{ K}_2\text{O}}{0.7 \text{ CaO}} \left. \begin{array}{l} \\ \end{array} \right\} 0.5 \text{ Al}_2\text{O}_3, 4 \text{ SiO}_2, 1 \text{ B}_2\text{O}_3$
3.  $\frac{0.3 \text{ K}_2\text{O}}{0.7 \text{ CaO}} \left. \begin{array}{l} \\ \end{array} \right\} 0.5 \text{ Al}_2\text{O}_3, 4 \text{ SiO}_2, 2 \text{ B}_2\text{O}_3$

The clearing-point of these glasses, that is, the point at which they become transparent, is about at cone No. 9. Frit No. 1 was found to be a perfectly clear glass, frit No. 2 was distinctly opalescent, and frit No. 3 was completely dimmed after cooling so that it was quite milky.

On grinding these with 10 per cent of Zettlitz kaolin and applying as glazes on a white ware body, the glaze from frit No. 1 had not yet fused transparent at gold-melting heat, No. 2 produced a transparent, glossy and shining layer, and No. 3 was still dimmed somewhat. According to this with an otherwise equal composition an increase in the content of boric acid brings about a dimming of the glaze; on account of the maximum melting-point of the glaze accepted it will hardly be

possible to go below 1 equivalent of boric acid to 4 equivalents of silica. Though the glazes higher in boric acid are more fusible, they are inclined to produce dimmed glazes. The alumina content of the glaze plays an important rôle here as in the other glasses.

The glaze frit,

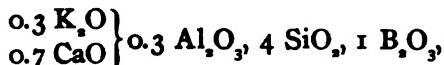


consisting of

	Parts
0.1 equivalent feldspar	27.85
0.2 equivalent potassium nitrate	20.20
0.7 equivalent marble	35.00
3.4 equivalents quartz sand	102.00
1.0 equivalent hydrous boric acid	62.00

resulted in a perfectly milk-white glass, opaque even in the fused condition.

Also the frit,

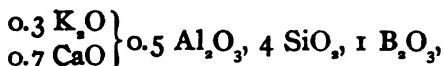


consisting of

0.3 equivalent feldspar	83.55
0.7 equivalent marble	35.00
2.2 equivalents quartz sand	66.00
1.0 equivalent hydrous boric acid	62.00

though transparent in the hot, fused condition, became dim even on quite rapid cooling, and assumed a milky appearance.

The glass, still higher in alumina, of the composition



was better in this respect. It was made up of

0.3 equivalent feldspar	83.55
0.2 equivalent Zettlitz kaolin	25.90
0.7 equivalent marble	35.00
1.8 equivalents quartz sand	54.00
1.0 equivalent hydrous boric acid	62.00

On slow cooling it showed but a slight opalescence.

A similar behavior was shown by a frit of the following composition, though here, owing to the increased content of silica, a brighter gloss was noticeable:

$0.3 \text{ K}_2\text{O}$	$\} 0.6 \text{ Al}_2\text{O}_3, 5 \text{ SiO}_2, 1 \text{ B}_2\text{O}_3$	Parts
$0.7 \text{ CaO}$		
0.3 equivalent feldspar	-	83.55
0.3 equivalent Zettlitz kaolin	-	38.55
0.7 equivalent marble	-	35.00
2.6 equivalents quartz sand	-	78.00
1.0 equivalent hydrous boric acid	-	62.00

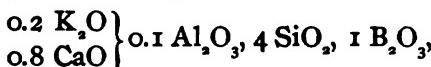
The two last frits, however, produced perfectly transparent and shining glazes when their alumina content was increased by an addition of 10 per cent of Zettlitz kaolin on grinding, but their melting-point was raised above that of the others discussed so far.

#### V. Glasses with an alkali-lime ratio of



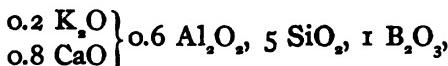
These behave practically like the glasses of the preceding group.

These also, with a composition of



produce a perfectly opaque white glass.

This glass, however, was cleared when the alumina content was raised to 0.3 and 0.5  $\text{Al}_2\text{O}_3$ , retaining otherwise the same composition. But the latter, as well as a glass, with a still higher content of alumina and at the same time an increased silica content,

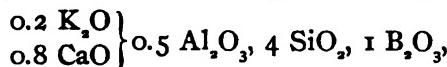


were dimmed somewhat more strongly than the corresponding glasses of the preceding group. A further addition of 10 per cent of Zettlitz kaolin removed this dimming completely in using the mixture as a glaze. A still further decrease in the alkali content, however, did not seem possible; when the alkali was lowered to 0.1  $\text{K}_2\text{O} : 0.9 \text{ CaO}$ , there were always obtained

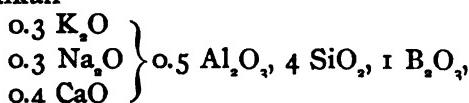
white milky glasses which, of course, were unsuitable for glazing, because they did not produce a transparent layer.

Collecting the results of this investigation, it is seen that the use of alkali-lime glazes is confined to much more narrow limits than the application of the lead glazes, and that much more care is necessary in their preparation in order that their composition may correspond to definite conditions. Yet it will be possible to replace a large number of lead glazes by such, free from this metallic oxide, containing lime. The greatest fluctuations are permissible in the ratio between lime and alkalies, and it seems of no moment which of the usual alkalies, potash or soda, is used. The proportions permissible lie here between a content of 0.2 equivalent potash or soda to 0.8 equivalent of lime, and 0.6 equivalent of potash or soda to 0.4 equivalent of lime. The different behavior of the glazes, high or low in alkali with respect to the body is, that glazes high in alkali are better suited for bodies containing much quartz, while those low in alkali are more suitable for a high alumina body.

The greatest peculiarity of lime glazes is the necessity of a very high content of alumina; without this, excepting the glazes corresponding in composition to ordinary glass, which, however, can be used only on a limited class of bodies, owing to the pronounced crazing on bodies high in alumina, dim and milky glasses will always be obtained. This will be true in a higher degree the greater the silica content is at the same time. A silica content of 4 equivalents will always be necessary in order to produce glazes possessing the required gloss. They require an alumina content of at least 0.5 equivalent. Expressed in percentage, this means that the glaze frit highest in lime,

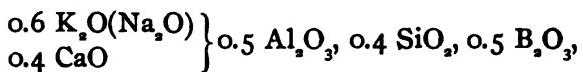


compounded with 10 per cent of the Zettlitz kaolin, requires in the glaze an alumina content of 14.8 per cent, while the frit highest in alkali

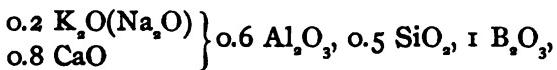


with an addition of 10 per cent of Zettlitz kaolin, an alumina content of 14.6 per cent. This would represent the minimum at all permissible. It has so far been believed that the alumina always tends to make glasses more dim and milky, and it has been considered risky to raise the alumina content so high. With lead glazes this seems indeed to be the case. This assumption is entirely incorrect, at least for the alkali-lime glasses. These, in fact, require a high content of alumina in order to produce transparent glasses at all on slow cooling; without it they become opaque. In the lead glasses hitherto used, the alumina hardly exceeded half the amount absolutely necessary for the lime glasses.

The content of silica in the lime-alumina glazes is likewise variable only within narrow limits. It is not permissible to go below 4 equivalents nor to exceed 5 equivalents. A lower content of silica changes the gloss of the glazes in a remarkable manner, a higher makes them difficultly fusible and at the same time makes necessary an additional increase in the alumina content. The content of boric acid must also not vary much. A boric acid content of 0.5 equivalent will be the lowest that can be used in order to keep the glazes from being too difficultly fusible, but a content of 1 equivalent must not be exceeded to any extent owing to the tendency of the glazes to become milky. Hence it will be necessary in working with lime-alumina glazes to keep the frits to be used within the limits



and



if it is not permissible to exceed the melting-point of gold, in order to insure success. One obstacle to the use of lime-alumina white ware glazes, to which I desire to call attention, is the high melting-point of the frits which makes it necessary to melt them at the highest temperature of the biscuit burns; and also, in my opinion, the fact that the frit kilns hitherto employed

(which empty themselves) cannot be used, since the high alumina frits are very toughly viscous, and hence are not inclined to run freely. In this respect a remedy could be found, however, by transferring the manufacture of the frits to separate establishments, where this is made a special business, as is done for the manufacture of white ware in England. In that country many potteries work entirely and advantageously with glazes which are produced on a large scale in other factories.

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### Persian Faience

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ALBERT BLEININGER, B.Sc., TRANSLATOR

In the collection of Persian art products which was made by the traveler, Dr. Ribbeck, and which was in 1884 exhibited in the art trade museum at Berlin, there was also a rich assortment of faience pieces. These were instructive in so far as they represent all the stages of manufacture and the manner in which they were made, by showing some of the products in the partly finished condition. A collection of these products has been placed at the disposal of the Royal Porcelain Factory, and some of the readers might be interested to obtain some information in regard to the raw materials used. The products consist of painted plates, jugs, pots, bottles, and candlesticks, as well as several painted building ornaments. Beside a few undecorated pots of a nearly white color, covered only with a colorless badly crazed lead glaze, presumably utensils for ordinary use, there are exhibited richly decorated pottery and building ornaments all of them executed in the same technique. They are made from a red burning clay covered with a white engobe which is painted in two blue shades with the oxides of cobalt and copper, the figures being leaf ornaments; the latter are covered with a magnificent turquoise-blue and a white transparent glaze which give to the articles a peculiar rough and a semi-glossy appearance.

The vessels are rather roughly turned by hand on the wheel, but their shapes possess a certain elegance. The white un-

decorated pots, which I have already mentioned above, seem to have been molded in rather rough molds, probably of burned clay, as is indicated by the seams shown. The red burning body is composed of a dark brown clay rather impure and poorly worked, and containing large grains of sand and a few pieces of marl. The body consists of

	Per cent
Clay substance	66.82
Calcium carbonate	2.50
Sand	22.02
Feldspathic residue	8.66

The body is covered with a white engobe which is applied to the raw, unburned piece. It is not finely powdered, and the grain may be seen and felt by rubbing with the hand. It covers the body smoothly and uniformly in a thickness of about 0.5 to 1 mm. The finest powder seems to have been removed by sieving or washing, for on being scraped off the body it produces a powder free from dust, but still consisting of very fine grains.

Owing to this condition it absorbs the colors which are applied very strongly and very uniformly. This seems to me to be an important point for such products, and to be well worth imitating. The engobe powder, however, would be removed very easily on touching and handling, because the sandy powder does not adhere firmly to the body; for this reason it is made up with an apparently large quantity of a vegetable mucilage which permits of handling the pottery and even of rubbing it strongly without injury. The engobe is very fusible; at silver-melting heat it becomes translucent, sinters together strongly, cracks and shells off. At a lower temperature corresponding about to our ordinary muffle heat, at about 700°, however, it adheres firmly to the body owing to incipient vitrification and becomes moderately dense. Its composition is as follows:

	Per cent
Silica	79.05
Alumina	2.83
Iron oxide	0.21
Lime	3.39
Barium	trace
Soda	10.82
Loss on heating	4.31
	<hr/>
	100.60

The loss on heating, due to organic, easily burned, substances, is to be ascribed for the largest part to the organic mucilage mixed with the engobe, perhaps also to a small addition of clay; otherwise the engobe apparently consists of a mixture of quartz sand and glass powder. Considering the lime and the alkalies which are contained in it in the insoluble condition as being constituents of a glass and assuming this to be an average two-and-a-half-fold silicate we will have to allow 35.27 per cent of the silica content for the formation of this silicate, and the total amount of the glass powder would thus amount to 49.48 per cent or approximately one-half. The layer of glaze is applied over the color which is painted upon the engobe in the raw condition; it could not be examined since none of the unburned substance rubbed from the vessels was available, but only the fused glaze in a very thin coating from which nothing could be removed by grinding. However it was possible for me to obtain some of the very beautiful opaque glaze on one of the building ornaments by grinding, which will give a basis for the glazes used on such products.

It had the following composition:

							Per cent
Silica	-	-	-	-	-	-	43.67
Alumina	-	-	-	-	-	-	2.84
Iron oxide	-	-	-	-	-	-	0.005
Lead oxide	-	-	-	-	-	-	25.51
Tin oxide	-	-	-	-	-	-	10.29
Copper oxide	-	-	-	-	-	-	4.96
Lime	-	-	-	-	-	-	0.79
Magnesia	-	-	-	-	-	-	0.17
Soda	-	-	-	-	-	-	8.62
Potash	-	-	-	-	-	-	3.74
							<hr/> 100.955

Considering the alkalies, the alkaline earths and the metallic oxides as the fluxes of a glass, but the oxide of tin as an acid replacing the silica, the glaze has nearly the composition of a bisilicate, for the proportion is calculated as follows:

$$\begin{array}{ccccccc} \text{Flux} & : & \text{Alumina} & : & \text{Silica} & : & \text{Oxide of tin} \\ 1 & : & 0.073 & : & 1.812 & : & 0.183 \\ & & & & & & \hline & & & & & & 1.995 \end{array}$$

The slight content of alumina is probably only an unintentional impurity.

The same glaze can be compounded from the following substances:

	Parts
Quartz - - - - -	44
Lead and tin ash - - - - -	36
Copper oxide - - - - -	5
Calcined soda - - - - -	12
Salt peter - - - - -	8

The ash required is obtained by calcining 24 parts of metallic lead and 8 parts of metallic tin. A glaze made according to this composition possessed exactly the same color and properties as the original Persian glaze. In the above glaze the amount of the alkalies to the lead oxide is as 0.35 is to 0.39; that is, almost the same. Now melting together lead oxide, soda, and quartz in the proportion of equal basic equivalents (that is, lead oxide, 111.5 parts, calcined soda, 53 parts, and sand, 120 parts), a glass is obtained which becomes liquid at a very low temperature. It is very easy to fuse to a smooth and transparent glaze already at muffle heat, 700°. Samples of Persian plates which were at my disposal in the painted but unglazed condition, on being coated in the raw condition with this glaze resulted in products which were exactly equal to the original, showing the same rough semi-glossy surface.

It is far from my intention to recommend to our industry the production of such wares; the pottery in the techniques peculiar to us is much more durable and much better; such decorated building ornaments might prove suitable and give rise to fine effects in the decoration of mosques and temples under an oriental sky, but in our northern climate they would not withstand the frosts of a single winter. Yet it is of some interest to follow up those techniques and to trace those methods of manufacture which from the purely technical standpoint we must regard as being behind the requirements of our times.

## Clay Mosaics

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ALBERT BLUMINGER, B.S.C., TRANSLATOR

At the Berlin Trades Exposition there was exhibited a new art industry which so far has not been represented in Germany, and owing to an unfavorable location, the same was not made very prominent, so that many visitors certainly passed the exhibit without paying attention to it. We mean the mosaics of artificial stone. Of late years increased attention has been paid to mosaic work as an architectural decoration, and a number of later Berlin buildings are witnesses of how they may be used for artistic purposes; we will mention here only the glass mosaic on the Victory column, the Pringsheim building on Wilhelm street, the National Museum, and the new railway hotel on Friedrich street. So far two kinds of mosaics have been distinguished, glass and stone mosaics. In the first the drawing was brought out by colored fragments of glass. In the latter naturally colored pieces of stone, especially of marble, were set together upon a surface corresponding to the shape of the wall or floor to be decorated and are then held together by pouring over them a cement, like asphalt, putty, plaster of Paris, hydraulic lime mortar, Portland cement, and thus putting together larger pieces.

The making of such mosaics is very laborious, and requires great skill and, neglecting the artistic value, becomes very expensive, owing to the manner of making the mosaic itself. The chipping and grinding of the small glass or marble prisms is a very laborious and slow process, and such decorations can hence only be used for artistic buildings of the highest class.

The new mosaic of artificial stone, which was exhibited at the Berlin Trades Exposition, in a few examples by Messrs. Th. Holzhueter and von Ratay, of Lichterfelde, is related in regard to the material used to the well-known mosaic tiles of the Mettlach factory of Villeroy and Boch. Though the various patterns of the latter products and the variety of colors made possi-

ble by them, together with their indestructibility, are an excellent means of producing mosaic-like effects, still, on the other hand, the division of the surface into smaller, square surfaces, and the necessary repetition of the pattern in a definite rhythm as well as the dependence of the architect upon the stock of patterns possessed by the manufacturer, are disadvantages which make a really artistic use more difficult. Messrs. Holzhueter and von Ratay, in proper appreciation of the excellent qualities of the Mettlach material, have made the attempt to use it in place of the fragments of glass or marble for the production of true mosaic, using small cubes of the same colored clay bodies constituting the Mettlach mosaic tile, and by their use producing mosaic pictures. These mosaics do not possess the brilliant colors and the iridescent gloss of the glass mosaic, but they do give rise when used in the right place to a very charming means of decoration. The clay cubes used are of 1 cm. edge, are pressed in molds to a sharp-edged shape and are burned very hard. The regular shape of these mosaics differing from the material used for glass and stone mosaic, causes chipping only occasionally, exact fitting being thus facilitated. The small cubes can be produced from the plastic mass comparatively much cheaper than in the case of the glass and stone mosaic. These circumstances permit the use of less skilled help and lower the price of mosaic very much as compared with the older methods.

In the small establishment for mosaic work which has been equipped by Messrs. Holzhueter and von Ratay at Licherfelde, the colored drawings which may also represent the different colors by numbers are spread upon a table in the manner of embroidery work, and are covered by girls with the colored clay cubes which, after being enclosed in a suitable frame, are covered with a layer of cement mortar. Tiles are thus produced in sizes up to a square meter which are joined together for floors and walks, and in which the colored cubes of clay bedded on the level surface, with very thin joints, represent a colored pattern. The mild colors and the comparatively cheap production of such mosaics admit of a more extensive use than the glass mosaic, especially for floors, and for this reason it has aroused the attention of

architects. A piece of work made by the small artistic establishment at Licherfelde, to which we wish to call the attention of those of our readers who are interested in such work, is the floor of the fountain basin in front of the National Museum representing waves and fish on a blue background for which the drawings were made by Architect Strack, and which were executed by von Ratay.

According to inquiries made by us the price of mosaic made from artificial cubes, amounts to from 20 to 60 marks per square meter, according to the richness of the design and the number of colors, while the price of glass mosaic is two to three times as high.

### III. ARTICLES TREATING OF REFRACTORY WARES

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#### Contributions to the Knowledge Concerning the Properties of Clays

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OTTO HENSEL, TRANSLATOR

In an older article<sup>1</sup> I pointed out that, in order to obtain a knowledge of clays for technical purposes, a manner of investigating clays other than the one now in vogue, is desirable. I called special attention to the investigations of clays carried on so far, as being of value only from special points of view, and to a large extent merely analytical exercises of very little use technically. In that article I particularly mentioned the mechanical analysis, an analysis by elutriation, as being useful, even essential, for arriving at a knowledge of the material. It will enable us to draw conclusions which are impossible to obtain from the simple chemical analysis, and which in most cases are of greater importance to the practical man than the purely analytical results.

On the study of its physical properties and the relations of these to the chemical composition of clay (which is called clay because peculiar physical properties cling to it, but considering the bulk of its composition is not entitled to the name in a chemical sense), no scientific treatise worth mentioning exists. Even Brogniart, who attended most assiduously to the study of its physical properties, is evidently on unknown ground for he is vague in his definitions and is in consequence obliged to append exceptions that cannot be explained.

Some experiments along the lines indicated by me, are indeed before us. Such are the labors of Malagutti on the change of specific gravity in Sevres porcelain during the different stages

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<sup>1</sup> "Deficiencies in the Examination of Brick Clays," *Notizblatt*, (1871) No. 4.

of firing, the results of which were confirmed by H. Rose with Berlin porcelain; the familiar work of Bischof and Richters on the connection between refractoriness and chemical composition, Bischof's scale of plasticity, detached notes on the amount of moisture which clays, completely dried, are able to absorb in an atmosphere saturated with aqueous vapor, determinations of the amount of silica that is present in clay either as combined silica, silica separated during the process of weathering, or as quartz incapable of change by weathering, by Forchhammer, Fresenius, Bischof, and others; tests on the extent of shrinkage in different materials and for various shapes, conducted at Sevres, and a considerable collection of gross analyses, in part of doubtful value. This, roughly, is perhaps all that has been done toward investigating the properties of a material so needful to man as clay is. Of all these, only the researches of Bischof and Richters have contributed to generalizations, toward formulating laws which may apply to all materials. The others are interesting for special cases, yet they do not, without further supplementary observations, permit of general application. From the results of these labors, few in number, and usually undertaken for special ends, it is impossible to establish laws.

If I meet with difficulties in studying the connection that surely exists between the physical and chemical properties, if I have been obliged even to discard some current views found in our technical manuals, because balance and rule have taught me otherwise, then it stands to reason that some properties of clays have not received very thorough investigation. In the work done so far, for instance, there is found nothing about the relation in which the porosity of the dried or burned clay stands to the amount of non-plastic contents and to its shrinkage; nothing about the force with which the clay retains its water during drying; nothing about the relation of the fineness of grain of the non-plastic matter to shrinkage, porosity, and the ability of clay to retain water; nothing about the relation of the chemical constitution of the natural non-plastic portion to the plastic portion; and other considerations of this kind.

Because of this want of data from which to start, it is ex-

tremely difficult to grasp properly the relations referred to, and their investigation has only just begun. Furthermore, these problems, whose solution I have undertaken jointly with Dr. Aron, present an ever-widening scope as we work on them; hence, no statement of the interesting results arrived at, need be expected, till these are in so complete a form as to be open for discussion.

This much is given as an introduction, to avoid giving the impression that the following publications on the plastic and non-plastic components of several clays, claim to treat the subject exhaustively. Still, I consider it expedient to give them to the public, since they prove that the views held thus far, concerning the relation in a chemical sense between the non-plastic and plastic ingredients of a clay, are in many instances not correct.

In all analyses so far published, either no notice is taken of the natural, non-plastic portions of the clay, generally designated as "sand," or the clay is conceived as a whole, or the sand has been separated either by elutriation or by chemical means; in the former case it appears in the analysis simply as sand, in the latter as "silica as sand" or "silica as quartz."

Now, the term sand is not chemically definable, since it means merely a state of aggregation in which *every* mineral may appear. If the clay is worked up in such a manner as to obliterate its earthy character by inducing complete fusion, in how far it is then permissible to throw together all the components, I have explained on a former occasion. As the amount of sand is very low in the highly plastic clays, it may here be considered as silica, since this mineral resists weathering more than any other, and always predominates, without falling into a serious error. It is different, however, with those clays which are termed lean, in which the sand exceeds the clay substance in amount, for a more careful examination of this component would be required in this case.

We know from the excellent work of Richters on the refractoriness of clays that different effects are produced, if (1) the silica of the clay is combined with other substances, or (2) is embedded as quartz grains. Silica alone is not fusible in the

most severe furnace-heat; it become so to the extent in which it combines with other substances, not excepting even alumina (infusible by itself). This combination, and the fusion keeping pace with it, does not take place until a temperature is reached higher than that at which a combination of the same substances formed or existing before, would assume the liquid state. The greater or less fusibility therefore not only depends on the chemical composition of the whole, but is vitally influenced by the greater or less resistance which the state of aggregation of the components opposes to chemical action; practice has known this for a long time, and without reasoning about it, increases the size of grain as far as compatible with other requirements. If materials of otherwise identical composition, with pure quartz as the non-plastic addition, exhibit such wide variations in their qualities, then this will be the case to a still higher degree if the non-plastic components are composed of fusible combinations along with quartz, as we may suppose to be true in the greater number of instances. In order to make plain this assumption, confirmed by but few direct tests, we must call to mind the origin of the clays, at least of all such as are not found on the site of the mother rock.

All those strata of the earth's crust that are designated as plastic clays, shales, pot clays, loams, brick clays, clayey marls, etc., and that preeminently furnish the raw materials for the ceramic industries, have come from the weathering of alumina-bearing rocks. Great differences in the mother rocks gave rise to differences in the properties of the products. Moreover, in addition to the mechanical disintegration by frost, by changes of temperature and by attrition, the chemical agencies of water and carbon dioxide, supported by alternately oxidizing and reducing influences, were at work in carrying off in soluble form single substances, especially the alkalies, lime, magnesia, ferric oxide, and manganous oxide.

The latter process concludes with the formation of those hydrated combinations of alumina that may be termed clay substance, the former with the formation of sand and mineral dust in all conceivable grades of fineness.

As both processes go on together, the non-plastic materials, that is, those portions proceeding merely from the mechanical wear and deposited in places where the transporting power of the water was less effective, will show all stages of chemical change and the coarser fragments will naturally contain a larger share of the undecomposed or undecomposable constituents of the original rock.

Let us bear the above in mind, in order to comprehend the manner in which I have arrived at the separation and designation of the mechanical components. It is now evident from the origin of clays, that they consist of grains admitting of measurement down to the finest, even of atomic size, in all gradations of comminution without abrupt gaps, as well as in all stages of chemical decomposition. The separation of such a mass into groups, can be carried out only in an arbitrary and conventional manner. The classification here adopted depends on such differences in the size of the particles, that each group exhibits special characteristics corresponding as closely as possible to qualities familiar to practice.

All the finest particles within a limit that can or ought to be maintained by the most careful washing on a large working scale, constitute clay substance. This exhibits the properties of the raw material intensified : highest plasticity, greatest affinity for water, high shrinkage and excessive cracking, and drying to a hard mass that takes polish. It was obtained by elutriation in a Schoene funnel by means of an ascending current of water flowing with a velocity of 0.2 mm. per second. The maximum size of grains corresponds to 0.01 mm. diameter.<sup>1</sup>

Those minute mineral fragments that can be worked with water like a short clay, but dry to a loose powder which takes no polish and, as a rule, neither shrinks nor cracks, are classed as rock flour. It is obtained at the velocity of 0.48 mm. per second ; maximum size of grains 0.25 mm. diameter.

Dust sand comprises those particles that no longer exhibit

<sup>1</sup> Schoene has calculated the diameter of the grains carried over from the velocity of the elutriating current, by assuming their specific gravity to be that of quartz.

plasticity when mixed with water, crumble when dried, and produce a grating sound when ground in the mortar, but give no sensation of grains when rubbed between the fingers. Velocity of the current is 0.99 mm. per second; size of grain, 0.04 mm.

Fine sand includes all grains from 0.04 to 0.2 mm.; coarse sand, all over 0.2 mm.

For the analysis, 50 grams of the clay dried at 120° were boiled with water for about an hour, the coarse materials as well as roots and other foreign admixtures taken out with a screen of 0.2 mm. mesh, and the balance was subjected to elutriation. After the finest portions, the clay substance, had been washed out, the remainder, that is the non-plastic components, was again subjected to boiling and elutriation; this process was repeated till the water flowed clear. Clays vary widely as regards the ease of separation; in the samples of Senftenberg clay, for instance, the clay substance was obtained by one boiling and washing; the operation had to be repeated four times with the Andennes clay.

Having removed the clay substance, the non-plastic portion was separated into particles of different size, as specified, by increasing the rate of flow. The samples, whose chemical analysis and that of the separate components is appended, had the following composition :

	I. Senftenberg, fat	II. Senftenberg, lean.	III. Senftenberg, medium fat.	Andennes
Coarse sand -	0.58	0.34	1.50	0.12
Fine sand -	3.00	28.46	8.80	0.68
Dust sand -	3.52	13.84	10.90	3.84
Rock flour -	11.16	20.24	12.88	4.26
Clay substance } (by difference) }	82.18	37.00	65.88	91.10
Total per cents	100	100	100	100

The chemical analysis of the substances obtained as above, was as follows:

## SENPENBERG CLAY OCCURRING WITH STRATA OF LIGNITE

	Plastic kind	Lean kind	Medium plastic kind			
	Raw clay	Raw clay	Clay substance	Rock flour	Dust sand	Fine sand.
Silica -	62.70	68.36	59.99	74.99	84.70	93.38
Alumina -	21.30	18.03	24.76	14.20	9.30	3.81
Ferric oxide	3.06	2.79	4.13	3.45	1.11	0.56
Lime -	0.58	0.72	} 0.93	0.18	0.27	0.10
Magnesia -	0.53	0.72		2.48	2.40	1.37
Potash -	2.18	2.24	} 2.48	4.60	2.33	0.76
Soda -	0.81	0.50		7.64	2.43	0.76
Combined water	8.57	7.54	99.93	99.83	100.14	99.98
	99.73	100.90				

## FIRE-CLAY FROM ANDENNES IN BELGIUM

	Raw clay <sup>1</sup>	Rock flour	Dust sand
Silica - - -	49.64	56.14	60.79
Alumina - - -	34.78	28.62	25.32
Ferric oxide - - -	1.80	3.11	3.18
Lime - - -	0.68	trace	trace
Magnesia - - -	0.41	0.61	0.30
Potash }	0.41	1.95	1.80
Soda }	12.00	9.57	8.61
Combined water - -	99.72	100.00	100.00

From the above figures of the chemical analysis, let us first draw conclusions in regard to the behavior of the clay in the fire. We know from the work of Bischof and Richters that the fusibility depends both on the ratio of the silica and alumina to the fluxes, and on the ratio between the first two; and that the fluxing elements exert an effect proportionate to their respective atomic weights. Calculating these relations,<sup>2</sup> we obtain:

<sup>1</sup> According to Bischof.

<sup>2</sup> We must bear in mind that in the above,  $\text{SiO}_3$  is the old formula for silica, and  $\text{FeO}$  that of the iron. Nevertheless, the value of the figures remains for purposes of comparison.

	Fluxes	Alumina	Silica	Sum of infusible elements
Clay substance of Senftenberg	1	2.55	7.25	9.80
Rock flour of Senftenberg -	1	1.92	11.10	13.02
Dust sand of Senftenberg -	1	2.10	21.77	23.87
Fine sand of Senftenberg -	1	1.61	45.92	47.53
Clay of Andennes -	1	6.86	13.26	20.12
Rock flour of Andennes -	1	3.65	8.05	11.70
Dust sand of Andennes -	1	3.71	10.05	13.76

In the Senftenberg clay we note how the amount of fluxes decreases and that of silica increases as the non-plastic components become more coarse-grained ; that in consequence the sand tends to resist the effects of heat more than do the finer portions of rock flour and clay substance. The opposite relation is noted in the Andennes clay ; here the non-plastic portions are more fusible than the raw clay, which is nearly all clay substance. To shed as much light as possible on these differences may prove of great importance to practice. Great variations appear in the physical character of separate layers of a clay deposit ; as the mechanical analysis of the Senftenberg clay illustrates, it is now the plastic clayey portion, now rock flour, now finer or coarser sand, that constitutes the bulk of the raw material. A knowledge of the properties of the separate components will therefore greatly aid in forming an estimate of the material.

Not only as regards refractoriness of different layers of a deposit, are these relations of significance ; they may also indicate variation in other properties that appear with a change of the mechanical composition. The size of grain in the non-plastic portions has much to do with the range of use and manner of working ; but these may also exhibit characteristics that give peculiar properties to the clay. As their chemically combined water indicates, the non-plastic portions of the Senftenberg or Andennes clay are not merely to be considered as rock fragments of various sizes or sand ; they have been attacked by the weathering process at a rate increasing with the fineness of grain. This chemical change has imparted to them some of the

properties of clay substance, although to a less degree. The ability to retain with great tenacity the water once taken up, is characteristic of clay substance, while sand readily parts with it by evaporation. We have no scale by which to measure this capacity of clay to retain water, but an index may be found in the avidity with which a clay draws moisture from the air, and condenses it within its pores. The different products of the elutriation furnish no less interesting hints on rapid drying than on refractoriness.

The samples dried at  $120^{\circ}$  to  $130^{\circ}$  and placed together with an open vessel of water under a bell-jar, consequently in an atmosphere saturated with aqueous vapor, had increased in weight by absorbing the following per cents of water:

Clay of Senftenberg: Clay substance 13.40 per cent, rock flour 5.39 per cent, dust sand 2.16 per cent, fine sand 0.4 per cent.

Clay of Andennes: Clay substance 26.17 per cent, rock flour 19.18 per cent, dust sand 17.95 per cent, fine sand none.

Although these figures cannot be used as standards of comparison (for the amount of water absorbed will depend on the temperature of the air and amount of water vapor present in consequence), the differences are so great that they deserve further attention; and I may revert to them in the future.

The tendency to crack more or less, which is another property peculiar to clays, seems to stand in some connection with differences in the constitution of the components.

The water being first siphoned off, the clay substance of both clays was poured as a slip-like mass on china plates, and in either case dried to a badly warped, hard disk with marginal cracks. As the dried cakes of the non-plastic portions of the Senftenberg clay neither cracked nor separated from the sides of the plates, they did not shrink; the same components of the Andennes clay, on the other hand, dried to prismatic pieces of a few millimeters diameter that crumbled on being touched gently. This striking difference in the behavior of the non-plastic portions seems to furnish an explanation of the fact that some clays, which may be lean and shrink very little, crack ex-

cessively, while others, when plastic and of high shrinkage, are much safer in this respect.

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### The Influence of the Constituents of Clay upon Its Fusibility

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OTTO HENSEL, TRANSLATOR

In former articles I, jointly with Dr. Aron, published a series of analyses of kaolins, plastic clays, and brick clays. Our principal aim was to call attention to the rational analysis, which up to this time was used only in pure science, and to show its value in practical testing and in determining the properties of clays, and especially its use in deciding on the composition of bodies. As is well known, certain branches of the clay industries do not always use clays alone, because these rarely give the desired qualities; but mixtures of one or of several clays with non-plastic and fluxing additions (sand, grog, quartz, flint, spar and other easily fusing minerals, slag, chalk, marble, marl, etc.), are commonly used for the bodies. Given the raw materials, the proportion of each is usually ascertained empirically, and frequently with great losses in the manufacture. On the constancy of this composition depends the certainty of results and pecuniary success; a small variation in the composition may impart very anomalous properties to the body: the color, ring, transparency, porosity, and elasticity of the ware, and the behavior in drying and firing may have changed so materially that great difficulties and losses result in the manufacture, and only the dump-pile grows in size.

As long as a concern takes proper care and obtains a supply of materials whose composition does not vary, there is no such risk after the first difficulties of empirical tests and trials. But it often happens that the raw material will vary in the deposit or will have to be obtained from another source. If in these cases the management wishes to avoid heavy losses in the manufacture, and tries to escape the many tedious empirical trials that

are often futile, a scientific control of the composition of the raw material is demanded.

The customary mechanical and chemical analyses of the raw materials in many cases may give useful hints, but do not always suffice to determine its properties with exactness. The practical man therefore regards the chemical analysis with a certain suspicion, often well-founded, because he cannot interpret it, or because the interpretation applied to it does not always harmonize with results looked for in practice. To form an idea of the significance of the chemical analysis in determining the properties of a clay, let us take the kaolins as an example.

The washed kaolins of commerce are not chemically uniform substances, but consist of a mechanical mixture of clay substance proper (the product of complete decay of feldspar), a feldspathic powder of extreme fineness, and quartz. Of the elements enumerated in the gross analysis of a kaolin, that is, silica, alumina, the alkalies, and the water, all but the last are present in components which are mineralogically distinct and unlike in properties. Silica is present in the free state as quartz (also in the amorphous or opal form) and in the combined state in the spar and the clay substance; alumina and the alkalies are present in the unweathered spar and the clay substance. If, therefore, the chemical analysis of one kaolin shows a higher percentage of silica than that of another, it does not necessarily follow that the former is more silicious, although this often is the case; it may as well be more feldspathic, since this mineral has a higher percentage of silica (70) and a lower of alumina (20) than the clay substance constituting the bulk of the sample.

It is at once evident to the practical man that a difference will result in a body having kaolin in its composition, when the high silica content of the latter comes from quartz or from feldspar or both. The customary gross analysis, merely giving the total of each elementary oxide present, affords no information on this point and admits only of conjectures, while here the rational analysis gives complete data since it enables us to ascertain the components, *i. e.*, the amount of quartz, feldspar, and clay substance and the chemical composition of the last one, sufficiently close for practical needs.

Examining the figures obtained by calculating the proportion of quartz, feldspar, and clay substance from the rational analysis of seven commercial kaolins we see that while the first two vary considerably between 35 and 9 per cent, the clay substance, notwithstanding the great differences exhibited by the gross analysis, shows a nearly uniform composition in all; we may hence deduce nearly identical properties for this substance in all kaolins. We are thus led to reason that the differences in the properties of kaolins are mainly due to the relative amounts in which the three mineralogical components are present,—components whose properties as distinct minerals are well defined.

For instance, ground feldspar and flint enter into the composition of china and white ware bodies. Hence it is important, when one kaolin is substituted for another, to know the amount of quartz and feldspar which they naturally contain. A variation in these two means a new body mixture—unknown to the manufacturer—and the assertion is not exaggerated that most difficulties of manufacture due to the behavior of the body, can be traced to variations in the composition of the kaolins—variations hidden to the manufacturer.

In the case of those sedimentary clays removed from the site of their origin (the plastic and brick clays, etc.), the results of the chemical analysis do not represent typical minerals very accurately. As their natural washing process was carried on, they were enabled to take up rock fragments foreign to the mother rock; and their clay substance (so named from its physical behavior) shows a more irregular composition than is the case with kaolins, and will therefore vary all the more in its properties. Nevertheless, the rational analysis gives excellent clues to an estimation of the properties of clays and of their behavior in the process of manufacture; it enables us to value properly the influence exerted on the whole by the components according to their respective amounts and character. Although this discussion of the rational analysis for clays and pottery bodies is familiar to the reader from the former articles referred to, I thought a repetition might be helpful in following my subsequent investigations on the effect of heat on clays and the phenomena connected therewith.

The analytical work mentioned in the introduction, caused Dr. Bischof to investigate the agreement between those analytical results and his proposed law of refractoriness—the fruit of years of laborious investigations on the connection between chemical composition and refractoriness or fusibility. In a comprehensive series of articles<sup>1</sup> he concludes that a well defined and striking influence of the separate components of kaolins and clays on their pyrometric value cannot be well detected, and that on this point the gross analysis is to be preferred to the rational analysis as a better guide. He believes himself justified in this inference, because the actual fusion tests agreed with his refractory law in most cases, and because he was unable to find a relation capable of numerical expression between the tests and the results of the rational analysis.

This was a surprise to me indeed. If he, by applying his law to the mineral constituents of a clay, had attempted to find an explanation for the seemingly contradictory behavior of the clays previous to complete fusion, it would have been easy to draw altogether different conclusions from the tests, especially for the lower temperatures, which are most important in practice and where his law breaks down completely. I consider this the only correct way. He would then have come to the conclusion with me that the rational analysis, in conjunction with the gross analysis, is not without its value in explaining the action of clays under heat, that it is capable of solving with ease many puzzling questions pointed out by him as exceptions to his law, still awaiting elucidation; and by extending the application of the refractory law, a valuable contribution to the investigation of clays would have been furnished. I have refrained from drawing these conclusions before, because I myself had not made any extensive series of tests in the same direction as Bischof did with the raw materials, used for analysis by me and for fusions by him; I wanted to convince myself to what extent such pre-conceived views as the observer may entertain, will influence the judgment in interpreting the signs of fusion. Before I give results and inferences I shall describe what physical and chemical

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<sup>1</sup> Thonindustrie Zeitung, 1877, Nos. 24 to 27.

changes take place in the firing of clays and how the separate components share in the process. Thus, in a sense, the refractory law will be assigned the limits of its operation. I consider this all the more necessary, as I differ with Bischof in interpreting the indications of fusion and in expressing his law numerically.

Recapitulating, the chemical changes wrought in clays by dark red heat, though differing very much in different clays, may be considered as a single operation. The expulsion of the chemically combined water stands foremost. Clay so burned can no longer bind water chemically, but draws it into its pores only in a mechanical manner and parts with it readily by evaporation at ordinary temperatures. Its characteristic property of forming a plastic mass with water is gone.

Such, at this stage, is the entire chemical change in the purest clays (the kaolins). In more impure ones (which embrace the great majority of clays), further manifold changes take place. Of the more common accessories, any organic substance present burns away; ferric hydroxide loses its water and changes to ferric oxide, which produces red coloring effects; pyrites (ferric sulphide), while yielding sulphur dioxide, and to some extent giving rise to sulphates, likewise becomes ferric oxide; the ferrous iron in the clay substance or in the sandy or dust-like rock fragments turns to ferric oxide; calcium and magnesium carbonates part with their carbon dioxide; other constituents, the quartz sand, feldspar, and similar detritus, that contain no combined water, remain unaltered. A chemical action of the particles on each other at low heats is entirely absent.

However various may be these changes in the accessory components of a clay, their effects, nevertheless, in almost every case are subordinate to the changes that have taken place in the clay substance, which is the cement of the heterogeneous elements; and just as in the raw state, it is the clay substance which, above all, has stamped its properties on the whole. The material has become harder, and is changed in color, though not in form. Its porosity is now considerably greater than it was when simply dried; it has been increased by the space which had been occupied by the substances evaporated.

The hardness of the burned clay stands in some relation to its plasticity, although the point has not been scientifically established. Ordinarily we may assume that clay burned at low heat increases in hardness with the unctuousness ("fatness") of the raw, plastic material.

This stage of the burn, however, will not, in most cases, satisfy practical demands, for the ware will now resist neither the destructive agencies of the atmosphere, vigorous pressure nor impact, nor will it retain fluids.

These properties are secured by a harder burn only when a portion of the constituent particles fuses and unites the remainder to a compact mass, rock-like to vitreous, according to the amount and nature of the melted particles. This process causes a shrinkage, due to the filling up of the pores, and this shrinkage increases with the amount of the mass that fuses and softens.

This stage, the vitrification of clays, includes two distinct processes: in the first, a wholly physical one, single components pass into the liquid state; in the second, a chemical one, substances unite to form new compounds having a lower fusing-point than the substances uniting. One instance will be given to illustrate the point. Although, as is well-known, lime in the pure state cannot be fused at all, and quartz only at temperatures unattainable in practice, both are used as fluxes in the composition of bodies. These are indirect means of fusion and vitrification, because they will, under right conditions, form a compound that is very fusible in comparison with the other ingredients.

To effect chemical combination, the most minute particles of the combining substances arrange themselves in a definite manner side by side. Mixing the substances ever so intimately will not be sufficient to induce combination. Chemical processes rather presuppose an unrestricted motion of the molecules, and never take place between two solid substances: one of these at least must be in a liquid or gaseous state. Hence, two solid substances will not produce chemical compounds, unless a liquid is present that will dissolve one or both of them, and thus

establish the proper contact. I may give an instance that can be tried by any one. If tartaric acid and sodium bicarbonate, both solids and soluble in water, are dissolved, and the solutions mixed, a violent reaction takes place; carbon dioxide is liberated and sodium tartrate is formed. On the other hand, mix these substances, in a perfectly dry condition, with all possible care, and no reaction takes place. Pour water on the mixture and a violent reaction at once begins. It is not even necessary, and it is well to bear this in mind in judging the behavior of clays, to add so much water as to dissolve all of the mixture; the least amount to start the mobility of the molecules will do, and if the mixture is merely set away in a moist place, reaction will take place.

This law, applicable to all chemical reactions between solids, must be held as valid for the mutual influence of the constituents of clays; until one of the natural compounds present has reached its fusing-point and thus, by its intermediation, is able to produce further chemical reactions,<sup>1</sup> an increase of fusing components by chemical action cannot take place.

In endeavoring to conceive of what will take place during the vitrification of a clay, it is, therefore, important to know which of its constituents is the most fusible and in what amount relative to the others it is present. We have not thus far been able to ascertain the fusing temperature of the components, separately considered, yet the application of Bischof's law will establish their relative fusibility, and the rational analysis their relative amount.

If we illustrate the process of vitrification in this way, that one or more of the components start fusion and in this state induce further liquid combinations, while the unfused portions

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<sup>1</sup> The influence of the greater or less fusibility of a component appears very clearly in the manufacture of cement. To produce Portland cement, a mixture of lime and clay is subjected to heat until it vitrifies to a mass like lava. The chemical composition of the very intimate mixture of these substances, finely powdered, must in all cases be nearly constant or may vary only within very narrow limits at most. According to Bischof's law, the invariable chemical composition of this mixture ought to require an invariable temperature of firing. In point of fact, the variation of finishing temperatures is considerable and depends on the fusibility of the clay employed.

constitute a rigid framework retaining the original shape of the article, then, at high temperatures, we must imagine the pores of the clay as more or less filled with liquid. If the molten portion represents only a small fraction of the whole mass, a greater hardness and slight shrinkage, without complete obliteration of porosity, will be produced. As the temperature rises and an increasing portion of the particles that represent the skeleton, liquefy, the pores fill more and more with fluid matter till, at the stage of vitrification of porcelain and paving brick, the pores are completely filled. As fusion beyond this point no longer enables the unfused portions to furnish a frame of the required rigidity, the articles lose their shape under their own weight.

If we speak of the fusibility of a clay from a practical point of view, this stage represents the highest temperature that is admissible, and tests at still greater heat are of little technical value, for the operation of burning always presupposes that the ware shall retain its shape. What takes place at temperatures beyond that may be of scientific interest, but is a matter of indifference to ceramic practice.

When the softening of the clay has progressed so far that the burned objects, by their loss of shape, are unfit for practical use, all of the mass has not yet become liquid, but the clay is now transformed into a viscous mixture of molten and unmolten substance, in which the former predominates. The fused portion does not chemically represent the entire clay (as Bischof's law assumes) until the mass runs in drops. If the particles of one of the unfused components happen to be larger than the rest and will therefore dissolve more slowly, the chemical composition of the fused mass and that of the clay will differ all the more, contrary to the assumption of Bischof's law.

All bodies capable of passing from the solid to the liquid state, do so at definite temperatures. Aside from slight variations due to conditions of pressure, these temperatures depend on their chemical nature.

With simple substances (*e. g.*, the metals) the temperature of fusion is one of the surest tests of their purity, as is also the

case with those compounds that are always obtained of a uniform composition (that is, all salts that crystallize). This law does not strictly apply, however, to the class of compounds regarded as so-called isomorphous salts, or compound solutions, which are formed when several simple or compound substances unite in any proportion in which they may be mixed, and give rise to new homogeneous substances, unlike chemical combinations proper in which the separate ingredients combine only in definite proportional amounts by weight, and where a deficiency or excess of one or the other remains in an uncombined state.

Instances of the first class, which behave in fusion in many respects like clay, are the mixtures of metals known as alloys, and the mixtures of salts of silica,—the common varieties of glass.

Most metals can be combined by heat in any desirable proportion, without again segregating according to their specific weight. These mixtures possess by no means the temperature of fusion that we obtain by calculating the proportionate amounts of the ingredients and the melting temperature of each, but experience shows that they are always more fusible than the mean of the ingredients would lead us to expect. In many cases, especially when a large number of metals have been united, the alloys are considerably more fusible than any of the ingredients. For instance, the four metals, tin, bismuth, lead, and cadmium, will produce an alloy that fuses at 80° (below the boiling-point of water), though the first two of the metals fuse above 200°, and the last two far above 300°.

The same peculiarity of a lowering of the fusing-point is exhibited by a long series of mixtures of salts that contain the same acid and the so-called double salts; mixtures of sodium and potassium carbonates or sulphates fuse much more easily than either salt.

The mixtures or compound solutions of salts of silica, the glass and glaze frits, act similarly, as workers in glass and glazes well know. Practice is aware of the fact that their fusibility depends not only on the ratio between the silica and the fluxes, but also on the nature of the flux (whether potash, soda, baryta,

alumina, lead, etc.), how many fluxes are used together, and in what proportion they are mixed. All these factors are of great influence. As a rule, with frits of the same degree of acidity, fusibility increases with the number of fluxes present. The proportion in which the fluxes are mixed will not by itself permit of positive conclusions as to fusibility. As in the fusion of clays, we have to deal with combinations similar to those in glass. The experience gained with the latter should be valid for the former.

The conditions in clays are more complicated, because here we have to deal not simply with the relation of the fluxes to one infusible element, silica, but also to another, namely, alumina, and the relation between alumina and silica also influence fusibility to an extraordinary degree. The confusion is still increased by a fact of the greatest consequence which is that in clays we are dealing not with a single chemical combination or a solution of chemical compounds, one in the other, but with a more or less intimate mechanical mixture, which, in the strict sense, cannot be expressed by a chemical formula; moreover, the physical state of the components prevents the transformation of the mass into a single homogeneous compound, until the clay has been fused to a glass; that is, until all the components of the clay as given by the rational or mechanical analysis, have lost their identity.

Bischof is therefore right in emphasizing repeatedly in his articles on the subject that the agreement between the theoretical fusibility found from the chemical composition, and the actual fusibility found by tests, holds good only when the firing temperature is very high,—at least the fusing temperatures from wrought iron to platinum, temperatures such as never occur in practice, and at which all clays except the most refractory, would be practically melted.

Hence, with the exceptions discussed above, Bischof's method will at most establish only what heat a clay will withstand before becoming a glassy mass. It does not at all permit conclusions as to its behavior at the temperatures commonly used in practice, and in most cases far removed from that of complete softening.

As stated before, we will meet great difficulties in determining in a scientific manner the correspondence between composition and fusibility; the influence of many factors has not been definitely determined, as for instance, differences in the physical condition, differences in the fluxes whether consisting of potash, soda, lime, iron, and in what proportion present. These must consequently be neglected. It is therefore evident that the theoretical refractoriness can be determined only approximately, especially as the point of fusion of a clay cannot be definitely fixed. Bischof's method, nevertheless, furnishes grounds for comparison and thereby becomes of some value. If we assume that it is true for all combinations of silica, its value will be positively increased, if it is not applied to the mechanical mixture of clay, but to the separate constituents, as the quartz and mineral fragments, and the other admixtures, which, taken separately, are homogeneous chemical compounds of definite fusing-point and properties. On the other hand, to speak of the fusing-point of the clay, is really out of the question. Applying Bischof's refractory law to the separate components of clays—as furnished by the rational analysis with sufficient exactness for practical needs, although not with scientific rigor—we can determine in what ratio the portions easily fusible, stand to the infusible ones that preserve the external shape of the object; also what relative resistance these will offer to the effects of heat, and what internal chemical changes of influence in the vitrification can be foreseen.

Although Bischof's refractory law suffers a restriction in its application, it can be given a larger scope in a direction that is of more value to practice.

Let us examine Bischof's refractory law for clays, by which a numerical expression is obtained from the chemical composition. We will not speak of the extensive experiments conducted by Bischof and Richters to determine the effect of the chemical constituents on the fusibility of clays, although in some respects of historical importance. A summary of the results, so valuable to the ceramic industries, will suffice.

All clays, aside from their mineralogical composition, con-

sist of silica, alumina, fluxes (potash, soda, lime, magnesia, the oxides of iron), and water. The last one and any organic matter present, do not enter into the consideration of refractoriness; but the iron oxide, in many respects allied to alumina in its properties, must be considered at high temperatures as an active flux.

The experiments of Bischof and Richters have shown that:

1. The degree of refractoriness of clays depends on the ratio which the fluxes bear to the refractory elements, the silica and the alumina.

2. The various substances that act as fluxes, exert a fluxing influence in the ratio of their equivalent (combining) weights; hence 20 parts of magnesia have the same effect as 28 parts of lime, 31 parts of soda, 36 parts of ferrous oxide, 47 parts of potash, etc.

3. The same amount of fluxes exerts a greater fluxing action on the clay when it is high in silica than when it is high in alumina.

4. The essential factor is the ratio between the silica and the alumina; clays are more refractory, as a rule, the more aluminous they are.

5. If the alumina is very low, it acts as a flux.

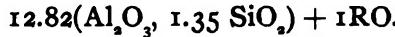
Bischof combines the figures of the analysis; he calculates the ratio of the silica and the alumina (first casting the different per cents into atomic expressions by dividing by the respective combining weights) to the sum of the fluxes, taken as unity, and next the ratio of the silica to the alumina.

For example, the well-known Zettlitz kaolin consists of



Hence the ratio between silica and alumina is 1.35 : 1.

He puts this into one expression by writing the pyrometric formula as follows :

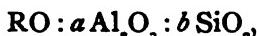


From these figures he obtains a single expression by dividing the ratio of the silica into the ratio of the alumina to the

fluxes (in this case  $\frac{12.82}{1.35} = 9.49$ ), and these last figures are styled the refractory quotient.<sup>1</sup>

The number thus obtained from the analysis by computation, indicates the place which a clay will occupy in the scale of refractoriness. The smaller it is, the less refractory the clay. When it is less than one, or is a proper fraction, Bischof no longer regards the clay as refractory, or as a fire-clay, and now obtains another number, named the "fusibility quotient." This is found by multiplying the alumina ratio, by the silica ratio; the number thus obtained grows larger as a clay is more fusible. The object has been to express in a single number what the experiment has revealed of the relations between silica, alumina, and the fluxes. Taking these figures for expressions of refractoriness or fusibility, as Bischof means them to be, let us examine them in reference to their increase or decrease, to see how far the results of the experiment have been expressed.

Following Bischof by expressing the facts of the analysis of a clay by:



the ratio of the silica to the alumina would be  $\frac{\beta}{\alpha}$ , and the pyrometric formula would be

$$\alpha \left( \text{Al}_2\text{O}_3, \frac{\beta}{\alpha} \cdot \text{SiO}_2 \right) + \text{RO}.$$

His refractory quotient (R. Q.) would therefore be

$$\text{R. Q.} = \alpha \div \frac{\beta}{\alpha} = \frac{\alpha^2}{\beta};$$

the fusibility quotient (F. Q.) for clays fusing easily would be

$$\text{F. Q.} = \frac{\beta}{\alpha} \times \alpha = \beta.$$

What we learn from this is that Bischof's refractory quotient increases as the square of the alumina ratio and decreases simply with the increase of silica, but that the fusibility quo-

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<sup>1</sup> This old quotient Bischof has replaced by a new one in which only the oxygen of the elementary oxides is used as a basis of computation, thereby increasing the result threefold.

tient expresses only the relation of the silica and fluxes,  $\text{SiO}_2 : \text{RO}$ , without regard to the alumina content.

Though experiments have shown that an increase of the alumina content contributes in a high degree to refractoriness, it has not been proved that this takes place in a quadratic ratio. The value of the R. Q. is simply dependent on the value of  $\frac{a^2}{b}$  and hence on the relation between the alumina and the silica, but the absolute amount of the fluxes as opposed to the infusible oxides is not expressed. On the other hand, in grouping the figures for the F. Q. for clays fusing easily, the relation in which the alumina stands to the other substances has been entirely eliminated from the expression.

It is at once obvious that the mutual relations, experimentally obtained, which silica, alumina, and the fluxes bear to the refractoriness of a clay, have been very imperfectly represented by Bischof's R. Q. and F. Q. The figures thus obtained can therefore be of service only in the comparison of clays whose chemical composition does not vary much, and only the fact of increase or decrease, not the rate of increase or decrease, as Bischof would assume, is conclusive. Besides, in the case of very silicious clays, the calculation of the refractory quotient, as Bischof has admitted, furnishes results incompatible with direct tests. Bischof's R. Q. would demand that with a steady increase of silica the refractoriness would be lowered,—an assumption that is contradicted by practical experience. Theory and practice coincide in these expressions only at such temperatures (it is necessary to repeat this) which do not interest practice, except in the case of earthy mixtures used as glaze materials.

As far as the experiments of Bischof and Richters will permit us to draw conclusions on the refractoriness of silicates of alumina, both on compounds purely chemical (clay substance of kaolins, feldspar, etc.), and with less reliable results on very intimate mixtures in which chemical action is not too much hampered by the physical condition (clay substance of the impurer clays), it can only be done if we oppose the fluxes to the

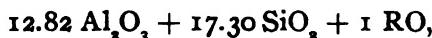
sum of the infusible oxides (silica and alumina) and multiply the sum of the two oxides by the ratio of the alumina to the silica. Thus we express the fact that refractoriness rises as the alumina increases, and falls as the silica increases. The simple ratio cannot, however, be taken, as both substances do not influence the fusibility to the same degree, but the value  $\frac{\text{Al}_2\text{O}_3}{\text{SiO}_2}$ , must receive a coefficient,  $y$ , that expresses by how much the influence of alumina exceeds an equivalent amount of silica. Finally, the whole expression must be increased by another factor,  $x$ , that expresses the varying effect of number and kind of fluxes present.

We may therefore express the refractoriness numerically as follows (and the experiments bear me out in this) by grouping the values obtained from the analysis to form one quantity :

$$\text{R. Q. (refractory quotient)} = x \left( (a + b)y \frac{a}{b} \right),$$

where  $a$  again represents the ratio of alumina, and  $b$  that of silica, to the fluxes, which are taken as unity. The value of  $x$  and  $y$  cannot be deduced from the data so far furnished by experiments. Omitting the unknown variables, we can obtain an expression valuable only for relative comparisons; but it, at least, exhibits what experiment has established as irrefutable, and it is applicable to all silicates of alumina whether fusing with ease or difficulty. The expression for the Zettlitz kaolin cited would be :

Pyrometric formula from the analysis :



$$\text{R. Q.} = (12.82 + 17.30) \frac{12.82}{17.30} = \frac{30.10}{1.35} = 22.29.$$

This calculation offers the additional advantage of considerably higher numerical results, whereby the differences brought out by the analytical data are set off more distinctly, which cannot be said of Bischof's calculation. In the subsequent experiments the expression calculated in this manner is always designated as R. Q. (S.) while that according to Bischof is R. Q. (B.).

The firing tests with the seven kaolins,<sup>1</sup> the porcelain body of Charlottenburg, four stoneware and four brick clays, which were repeated, were conducted somewhat differently from Bischof's. His object was to establish the absolute resistance of the clays to high temperatures, while I endeavored rather to note sharply the stage where fusion just begins,—the incipient vitrification.

Instead of Bischof's test-pieces of cylindrical shape, I molded small three-sided pyramids with basal edges of 1 cm. and a height of 3 cm. in a metal mold of accurate workmanship. They were burned at a low heat before being subjected to the tests. Because of their sharp apex and edges these pieces show any changes more distinctly than do Bischof's. Eight of such pyramids were stuck together on a fire-clay plate for the test, repeatedly exposed to heat that was carried higher at each repetition, and the changes they had undergone were noted at each repetition. With every new increase of temperature,<sup>2</sup> those pieces that by their bending had shown complete softening were omitted, as they would have run over the others and spoiled them.

Bits of two different metals placed in small crucibles of Zettlitz kaolin in the center of the ring formed by eight test-pieces, were used to determine the temperatures obtained. The metals employed were: brass (fusing-point at about 900°); silver (1000°); copper (1100°); cast-iron (1200°); steel (1400°); wrought iron (1600°); platinum (2500°). The temperatures given in the appended tables therefore refer to the fusing-points of these metals.

The results of the fusion tests are arranged in two tables: one for the kaolins and the other for the potter's and brick clays; the results of the chemical analysis have been added for reference.

<sup>1</sup> The analyses of these clays, together with pertinent observations and deductions, are given in the chapters "On the Chemical Constitution of Clays," and "Contribution to a Better Knowledge of the Kaolins." "On the Chemical Constitution of Plastic Clays," also bears on the subject.

<sup>2</sup> Firing to temperatures just above the melting-point of wrought iron, was conducted in a wind-furnace fired with coke, the pieces being placed in a small round saggars. For higher temperatures a Deville furnace like Bischof's was employed.

TABLE I. FUSION TESTS

Name	Composition in per cents	Temperature <sup>1</sup>	
		(Silver fused) 1000°-1200° C.	(Cast iron fused) 1200°-1400° C.
1. Kaolin from Ledets.	Clay subet. 88.26 Spar 8.66 Quartz 3.08	Shape: retained Surface: dead Fracture: earthy, dusting off Edges: not translucent	retained dead earthy, somewhat harder not translucent
2. Kaolin from Kottiken.	Clay subet. 87.41 Spar 6.19 Quartz 6.40	Shape: retained Surface: dead Fracture: earthy, dusting off Edges: not translucent	retained dead earthy, somewhat harder not translucent
3. Kaolin from Tremosna.	Clay subet. 90.29 Spar 5.63 Quartz 4.08	Shape: retained Surface: dead Fracture: earthy, dusting off Edges: not translucent	retained dead earthy, somewhat harder not translucent
4. Kaolin from Zettlitz.	Clay subet. 96.55 Spar 1.15 Quartz 2.30	Shape: retained Surface: dead Fracture: earthy, dusting off Edges: not translucent	retained dead earthy, somewhat harder not translucent
5. Kaolin from Lettin.	Clay subet. 74.08 Spar 8.70 Quartz 17.21	Shape: retained Surface: dead Fracture: earthy, dusting off Edges: not translucent	retained, shrinkage evident dead denser grain, hardly absorbent somewhat transl.
6. Kaolin from Kaschkau.	Clay subet. 78.51 Spar 0.59 Quartz 20.90	Shape: retained Surface: dead Fracture: earthy, dusting off Edges: not translucent	retained dead earthy, dusting off not translucent
7. Kaolin from Sennewitz.	Clay subet. 63.77 Spar 0.75 Quartz 35.50	Shape: retained Surface: dead Fracture: earthy, dusting off Edges: not translucent	retained dead earthy, dusting off not translucent
8. Porcelain body of Royal Porcelain Works Charlotteenburg.	Clay subet. 54.92 Spar 21.56 Quartz 23.52	Shape: retained Surface: dead Fracture: earthy, somewhat harder Edges: not translucent	retained, shrunk with mat luster almost perf. dense, coneoidal fairly translucent

<sup>1</sup> Attention is called to the fact that the temperatures approximated are taken too high according to later researches.—ED.

WITH THE KAOLINS

Temperature			R.Q.(S)	R.Q.(B)	R.Q.(B) of whole
(Steel fused) 1400°-1600° C.	(Wrought iron fused) above 1600° C.	(Platinum fused) 2500° C.	of clay sub- stance		
retained dead  conchoidal, some- what vitreous hardly translucent	retained appears barely glazed vitreous, slightly lustrous slightly translucent	somewhat sagged glossy full of small pores sharp, fairly trans.	34.26	15.04	8.60
retained dead  conchoidal, some- what vitreous hardly translucent	retained appears barely glazed vitreous, slightly lustrous slightly translucent	somewhat sagged appears barely glazed full of small pores somewhat rounded fairly translucent	36.79	16.12	9.43
retained dead  conchoidal, some- what vitreous hardly translucent	retained appears barely glazed vitreous, slightly lustrous slightly translucent	strongly warped appears barely glazed full of small pores much rounded, fairly translucent	21.12	9.16	6.46
retained dead  conchoidal, some- what vitreous hardly translucent	retained more mat than those above vitreous, slightly lustrous slightly translucent	unchanged appears barely glazed full of small pores sharp, fairly trans.	24.30	10.64	9.43
retained  dead conchoidal, vitre- ous fairly translucent	retained  somewhat lustrous vitreous and con- choidal fairly translucent	much warped and sagged pitted, glazed full of small pin- holes hardly translucent	14.09	6.04	3.00
retained  dead earthy, still absor- bent not translucent	retained  dead still somewhat ab- sorbent hardly translucent	not changed; sharp edges pitted, glazed full of small pin- holes hardly translucent	29.40	12.72	7.88
retained with mat luster  conchoidal, very much denser fairly translucent	retained  somewhat lustrous conchoidal, dense fairly translucent	completely run and spread as white enamel full of holes	10.98	4.63	1.97
retained with mat luster  perfectly dense, like china very translucent	retained  somewhat pitted, touch of glazing full of fine pores less translucent	completely spread as a compact glass  translucent green- ish white	10.29	4.31	1.31

TABLE II. FUSION TESTS WITH

Name	Composition in per cents	Temperature		
		(Brass fused) below 900°-1000° C.	(Silver fused) 1000°-1100° C.	
1. Clay from Greppin.	Clay substance Feldspathic minerals Quartz	79.42 6.28 14.30	Shape: retained Surface: dead, porous Fracture: earthy, somewhat hard, whitish yellow	hardly altered
2. Clay from Liegnitz.	Clay substance Feldspathic minerals Quartz	46.52 6.00 47.48	Shape: retained Surface: dead, very porous Fracture: earthy, less hard than foregoing	hardly altered
3. Clay from Kottiken.	Clay substance Feldspathic minerals Quartz	72.21 4.73 23.06	Shape: retained Surface: dead, porous Fracture: earthy, somewhat hard, whitish yellow	hardly altered
4. Clay from Ledetz.	Clay substance Feldspathic minerals Quartz	62.03 2.89 37.97	Shape: retained Surface: dead, porous Fracture: earthy, somewhat hard, whitish yellow	hardly altered
5. Clay from Rathenow.	Clay sub. 64.13 } Feld. min. 12.70 } Quartz	76.83 27.12	Shape: retained, strongly absorbent Surface: dead Fracture: earthy, somewhat hard, brick-red	hardly altered, somewhat darker red
6. Paving brick clay from Bockhorn.	Clay sub. 44.06 } Feld. min. 14.06 } Quartz	58.12 44.88	Shape: retained, strongly absorbent Surface: dead Fracture: earthy, somewhat hard, brick-red	hardly altered, somewhat darker red
7. Paving brick clay from Schwarz-hütte.	Clay sub. 29.99 } Feld. min. 19.37 } Quartz	49.36 50.64	Shape: retained, very porous Fracture: earthy, barely cohering, brick-red	hardly altered, somewhat darker red
8. Clay from Christiania.	Clay sub. 49.03 } Feld. min. 32.64 } Quartz	81.67 18.33	Shape: retained, porous Fracture: earthy, somewhat hard, flesh-tinted	Shape: retained Surface: dead Fracture: nearly non-absorbent reddish brown

PLASTIC AND BRICK CLAYS

Temperature				R.O.(S)	R.O.(B) of clay sub- stance	R.O.(B) of whole
(Copper fused) 1100°-1200° C.	(Cast iron fused) 1200°-1400° C.	(Steel fused) 1400°-1600° C.	(Wrought Iron fused) above 1600° C.			
Shape: retained Surface: mat luster, yellowish brown Fracture: nearly non-absorbent Edges: slightly translucent	As before, but deeper brown	Shape: almost completely retained Surf: gray-brown gloss, blistered Fracture: finely porous Edges: not trans.	Shape: recognizable but badly swelled Edges: rounded	4.63	1.86	1.30
Shape: retained Surface: dead Fracture: earthy, strongly absorbent, yellowish white	Shape: retained Surface: dead, gray Fracture: porous, distinct grains Edges: not translucent	Shape: somewhat sagged and swelled Surface: slightly glazed Fracture: appears like sugar Edges: somewhat rounded	Puffed up to a spongy mass Edges: disappeared	3.31	1.07	0.40
Shape: retained Surface: dead, whitish yellow Fracture: earthy, absorbent Edges: not translucent	Shape: retained Surface: dead, whitish yellow Fracture: grains compacted, barely absorbent Edges: slightly translucent	Shape: retained Surface: barely glossy Fract.: highest density of grain (non-absorb.) Edges: slightly translucent	Shape: retained Surface: slightly glazed Fracture: with pore-like holes	8.70	3.72	2.03
Shape: retained Surface: with slight luster Fracture: non-absorbent Edges: somewhat translucent	Shape: somewhat swelled Surface: glazed, blistered Fracture: fine pin-holes Edges: much rounded	Puffed up to scoriaceous slag, full of large holes	Spread to a gray enamel	3.29	1.91	0.59
Shape: swelled Surface: slightly glazed Fracture: brownish red, vesicular Edges: fully rounded	Kept out of test			1.21	0.63	(4.17)
Shape: retained Surface: slightly glazed Fracture: highest density of grain, reddish brown, glossy	Spread to brown enamel			1.44	0.52	(5.12)
Shape: retained Surface: dead Fracture: nearly non-absorbent, reddish brown, slightly glossy	Shape: much sagged Surface: glazed Fracture: scoriaceous Edges: fully rounded			0.71	0.19	(6.05)
Melted to slaggy ball with large vesicles	Kept out of test			0.96	0.31	(2.79)

On comparing these results with the data of the analyses, it becomes evident at once that the degree of vitrification and that of the final softening depend on the substance that predominates (that is, clay substance), but that the refractory influence of the latter is vitally modified by the amount of feldspathic fragments, and, in case the quartz is accompanied by a noteworthy amount of feldspathic matter, the quartz as well. The clay substance of the several kaolins, assumed by Bischof as uniform in refractoriness, and therefore set against the mineral fragments simply with reference to the amounts present but neglecting its refractory quality, varies much in this respect, as the refractory quotients run from 36.79 to 10.29. In studying the results of the fusion tests, this point must not be neglected, as this component greatly overshadows the others.

Up to the highest temperatures those kaolins, which are nearly or wholly free from feldspar, and whose clay substance is highly refractory, have fully preserved their shape,—those of Kaschkau and Zettlitz; next in rank are those that with a clay substance, equally or more refractory, contain large amounts of substances fusing easily as spar and quartz, etc.,—those of Ledetz, Kottiken, and Tremosna; those with a clay substance of lower refractoriness come last,—those of Lettin and Sennewitz, which latter is also an ingredient of the porcelain body of Charlottenburg.

Not only for the highest temperatures (rarely obtained in the industries), but also for the lower degrees of heat customary in practice, does the amount of feldspar present furnish a valuable index as to the course which the vitrification will take, and especially if the quartz content is considered in connection with it. That the quartz does not always act as a flux is proved by the tests. Its effect commences with the fusion of the feldspar which, when in the liquid state, is capable of dissolving silica, as is well known, and in this manner the quantity of the fluxes will be increased; but in the absence of feldspar or other substances of low fusing-point, it imparts higher refractoriness to the kaolins, as shown by those of Sennewitz and Kaschkau; in this case it cannot begin to act as a flux until the clay substance softens.

It is widely held that the porcelain body of the Royal Porcelain Works requires a high finishing heat, perhaps the highest among the German porcelains, approaching the fusing-point of wrought iron. As it contains the kaolin of Sennewitz as the most refractory element, whose clay substance is relatively more fusible than the same constituent of other kaolins, we may well take for granted that the clay substance of all materials investigated affords in the amount present a sufficiently firm skeleton to preserve the shape of articles, so far as practical requirements are concerned, and that only such porcelain bodies will prove more fusible which contain a large percentage of fluxes. It will therefore be of much greater practical value to know the amount of fluxes naturally contained in the kaolins than to know their absolute fusing-points.

In an interesting inquiry on the part that quartz plays as an ingredient of porcelain bodies, A. Buenzli (1876) has found with the aid of the microscope that at high temperatures feldspar will dissolve a considerable quantity of silica to form a clear homogeneous glass. The amount of dissolved silica increases with the rise in temperature till, in the finishing heat of the porcelain kiln, it is equal to the silica originally held in combination in the feldspar; it is likely that still higher heat will further increase the capacity of feldspar of dissolving quartz. He also found that even amorphous silica, which is more easily attacked than quartz, is not taken up at all at temperatures but little exceeding the fusing-point of feldspar. From my own observations I can substantiate this result. According to these, reserved for a later report, a dissolving action of feldspar on quartz was not positively established for a temperature between the fusing-points of cast iron and steel, but it was found to be very pronounced at a greater heat, approaching the fusing-point of wrought iron, and the combination produced a glass that was decidedly more fluid than pure feldspar is for the same temperature. But we would be wrong if from the greater fluidity of this more acid silicate we should infer an easier fusibility (*i. e.*, an earlier softening for a mixture of feldspar and quartz); still we may take for granted that when chemical action between feldspar and

quartz has begun at a sufficiently high temperature, then not only the greater quantity of liquid matter but also its increased mobility must have an influence on vitrification and the loss of porosity ; and progressive chemical reactions that we must suppose as occurring between quartz and clay substance at still higher temperatures, will also be promoted.

In what manner feldspar reacts with clay substance, if it does so at all, has not as yet been investigated ; from analogies before us on the behavior of molten glass with plastic clays and with quartz materials, we may reason that either no reaction takes place or it is much weaker than between feldspar and quartz. It may rather be assumed that clay substance, being a basic silicate of alumina, has a strong tendency to combine with more silica, just as feldspar does. The solid state of both bodies at very high temperatures is an obstacle to a chemical reaction and it is shown by my experiments, as well as by those of Bischof previously published, that a greater heat is required for quartz to exert its fluxing action if the clays, taken as a whole, are more refractory. In the process in which the quartz liquefies the refractory clay substance, the content of feldspar must necessarily be an important factor as the latter furnishes a solvent for the quartz and thus brings it into a form capable of reacting, according to general chemical principles. The greater or less energy which quartz displays as a flux, will therefore depend essentially on the amount of feldspar that accompanies the clay substance in the kaolins.

From this it appears that as regards refractoriness, neither the quartz alone, nor the feldspar by itself, will turn the scales. This depends in the first place on the refractory quality of the clay substance. The first two can lower the refractoriness only according to quantity and proportionate amounts present.

All factors, feldspar, quartz, and clay substance, are therefore entitled to equal consideration, and the various influences, now opposing, now augmenting each other, cannot be precisely expressed by one value (refractory quotient), even if it can be made to coincide with the facts in some cases.

If we arrange the kaolins tested into a series according to

the degree of softening they have undergone at the highest temperature employed (as far as their condition will permit of an objective comparison, since small differences and accidental changes are liable to different subjective interpretations), and compare this series with the refractory quotients calculated separately for the clay substances and for the entire clays, we are able to obtain a very good picture of the influence of the separate components, even though from the nature of the case it cannot be expressed numerically. The kaolin of Kaschkau is most refractory,<sup>1</sup> and the body of Charlottenburg is the least refractory.

On the whole, this series agrees with Bischof's tests, if it is borne in mind that the differences among the kaolins of Zettlitz, Kottiken, and Ledetz are so insignificant as perhaps to give rise to a different arrangement in the hands of another observer.

	R. Q. (S.) of clay substance	R. Q. (S.) of the kaolin as a whole	Contents in	
			Feldspar	Quartz
Kaolin of Kaschkau	29.40	19.56	0.59	20.90
Kaolin of Zettlitz	24.30	22.54	1.15	2.30
Kaolin of Kottiken	36.78	24.36	6.19	6.40
Kaolin of Ledetz	34.26	21.74	8.66	3.08
Kaolin of Tremosna	21.12	16.48	5.63	4.08
Kaolin of Lettin	14.09	9.56	8.70	17.21
Kaolin of Sennewitz	10.98	8.12	0.75	35.50
Charlottenburg body	10.29	5.13	21.56	23.52

We observe that the refractory quotients of the clay substance in the kaolins of Kottiken and Ledetz are the highest of all, and that the same is true, but to a slightly less degree, of the kaolin of Tremosna. If they occupy only the third to fifth place in the scale, this is due to their moderately large content of spar and quartz. Such a large amount of spar and quartz is capable of bringing a large share of liquid substance into the pores at lower temperatures and thereby facilitating a greater

<sup>1</sup> As the materials of the crucibles that Seger employed in the experiments did not permit firing to the extent of complete fusion of the test-pieces, it must remain an open question whether for temperatures of actual fusion the series with the kaolin of Kaschkau at the head, really tells the truth.—Editors of German edition.

mobility of the clay particles at the higher temperatures. The kaolin of Kaschkau, in spite of its lower R. Q. and the high quartz content, lacks the vehicle feldspar, that has to accompany quartz to make it a flux, and hence retains its first place.

The refractory quotients of the clays calculated in both ways, after all show a sufficient agreement with the practical tests; and we may recognize that the assumption of a homogeneous or nearly homogeneous fluxing (an assumption I held necessary for the application of the quotients) comes true, with the exception of the kaolin of Kaschkau.

It will be impossible to find such an agreement if we stop at the first signs of fusion at lower temperatures. The first signs of fusion consist in a hardening of the mass, and next a shrinkage, a condensing of the grain, the fracture becoming conchoidal and vitreous, and the edges translucent. Let us now arrange the kaolins according to their priority in exhibiting these signs and we see that their succession differs from that of complete fusion, and that there is no connection between the two. In this table the kaolin that first exhibits the signs of fusion stands at the head, and so on, until the last in the list, which is last to show signs of fusion.

		Feldspar	Quartz	R. Q. (S.)	R. Q. (B.)
Body of Charlottenburg	-	21.56	23.52	5.13	1.31
Kaolin of Lettin	-	8.70	17.21	9.56	3.00
Kaolin of Ledetz	-	8.66	3.08	21.74	8.60
Kaolin of Kottiken	-	6.19	6.40	24.36	9.43
Kaolin of Tremosna	-	5.63	4.08	16.48	6.46
Kaolin of Zettlitz	-	1.15	2.30	22.54	9.43
Kaolin of Sennowitz	-	0.75	35.50	8.12	1.97
Kaolin of Kaschkau	-	0.59	20.90	19.56	7.88

Here again it remains a question, what place shall be assigned to the kaolins of Ledetz, Kottiken, and Tremosna with reference to one another, as differences can hardly be observed.

In this table the effect of feldspar is very pronounced. It shows that the lowering of the temperature, when this process begins (*i. e.*, the closing of the pores, the changing of the appearance of the fracture to vitreous, the translucency of the edges), and the

intensity of its action, are proportionate to the amount of feldspar present, and stand in no relation to the absolute refractoriness of the clay. The characteristic behavior of the separate components will serve to explain this. Accepting the normal composition of feldspar to be expressed by the formula  $RO + Al_2O_3 + 6SiO_2$ , we would indicate its fusibility by the number  $(1+6)1/6 = 1.16 R. Q. (S.)$ . The refractory quotient of the clay substance in the Sennewitz kaolin, the most fusible of the lot, is expressed by 10.98 (or 10.29, when obtained and calculated from the porcelain body). A great interval separates these values : the spar, in point of fact, exhibits pronounced signs of softening at a temperature lying between the fusing-points of copper and cast iron, but the Sennewitz kaolin does not show the least signs of fusion at a considerably higher temperature. Spar must hence begin to fuse in every kaolin in which it is present, when its fusing-point is reached. By filling the pores according to its amount, it shows its effects by a cementing of the unfused portion.

The quartz does not enter into chemical action till far above the fusing-point of feldspar, which dissolves the quartz, as we have seen, and thus increases the bulk and becomes more fluid. Hence we also observe that the compacting of grain and the translucency, and in part the appearance of lustrous surfaces, increase proportionately more rapid as the kaolin contains an abundance of quartz along with the feldspar. By referring back again to the large table, we arrange the kaolins with reference to the signs of accelerated fusing action in the order of rapidity, placing the body from Charlottenburg, which showed the most rapid increase of vitrification, at the head :

	Spar	Quartz
1. Body from Charlottenburg	21.56	23.52
2. Kaolin of Lettin	8.70	17.21
3. Kaolin of Ledetz	8.66	3.08
4. Kaolin of Kottiken	6.19	6.40
5. Kaolin of Tremosna	5.63	4.08
6. Kaolin of Zettlitz	1.15	2.30
7. Kaolin of Sennewitz	0.75	35.50
8. Kaolin of Kaschkau	0.59	20.90

It is to be observed that the fluxing action of the quartz depends essentially on the presence of feldspar; but in those kaolins which contain very little or no spar, it stands in direct relation to the fusibility of the accompanying clay substance. This becomes especially striking on comparing the three poorest in spar:

	Clay substance	Quartz	R. Q. (S.) of clay substance
Kaolin of Sennewitz -	63.77	35.50	10.98
Kaolin of Zettlitz -	96.55	2.30	24.36
Kaolin of Kaschkau -	78.51	20.90	29.40

The kaolins of Sennewitz and Kaschkau contain the least spar and the most quartz; they also have retained the porosity of structure longest of any, and at the earlier stages of firing they are the ones most difficult to vitrify. Although the Sennewitz kaolin is the most fusible at the highest temperatures, both as to its clay substance and the whole mass, it does not begin to vitrify any sooner than the far more refractory one of Zettlitz, which is nearly pure clay substance (96.55 per cent). From this it follows that the fluxing action of quartz (which takes place very rapidly in the Sennewitz kaolin with the rise in temperature, because of the great quantity present), begins only when the clay substance commences to soften. In the Kaschkau kaolin with its much more refractory clay substance, the action of the quartz sets in correspondingly later,—in the Sennewitz kaolin below, and in the one of Kaschkau above, the fusing-point of wrought iron.

Thus the varying and fusing effects of quartz find a natural explanation.

The changes produced by a progressive rise of temperature, have been discussed very fully for the kaolins, as they are exhibited here more distinctly and simply than is the case when noting the same changes in impurer materials,—the secondary deposits of plastic and brick clays.

In the kaolins the same mineral components (quartz, feld-

spar, and clay substance) occur together; their characteristic properties vary but little, notwithstanding diversities of the mother rocks, and their proportionate amounts can be determined with almost scientific exactness.

The kaolins vary but little in physical properties and, when washed, are all of the same plasticity, of almost the same hardness after a soft burn, of the same color, etc. They furnish a good subject for the experiment, because the changes they exhibit are identical and differ only in degree.

In the impure clays (the plastic and brick clays) the conditions are much more complicated. Here that portion designated as clay substance is not a purely chemical compound of nearly uniform composition, as in kaolins, even though physically homogeneous. It is not produced from the decomposition of a single well-known mineral. It may be a mixture derived from the weathering of various very unlike minerals and accompanied by minute undecomposed rock fragments — fragments that share, with the products of chemical decomposition, the distinguishing quality of dissolving in sulphuric acid. The truth of this applies to clays in proportion as they are denominated more impure. That portion, also, described as "feldspar," will not always be identical with the substance of the same name in kaolins; it will consist largely of other mineral detritus which has merely the high percentage of silica in common with spar, and for that reason is not decomposed by sulphuric acid. These clays, now to be discussed at length, differ from one another in a variety of ways: in plasticity, hardness after drying and soft burning, size of grain, color, and the total absence of translucency in the case of some when vitrified.

It is obvious that the phenomena accompanying the process of fusion do not permit of so lucid an insight into the influence exerted by the mechanical constituents. We will also see that they are less adapted for establishing direct comparisons, and that single indications may be confusing, especially since the rational analysis in these clays does not furnish such definite data with regard to their composition as were obtained from the kaolins.

The rational analysis nevertheless offers fairly good explanations for what takes place in burning, as we shall see from the following firing tests.

In the more fusible clays (the plastic and brick clays), the separate components present conditions of fusibility that depart very much from those found in the kaolins.

In the latter, the clay substance, both with respect to quantity and its high refractoriness, constitutes the material that composes the stable framework which preserves the shape of the object, while the feldspathic matter preeminently induces a compacting of the mass (the closing of pores) by reason of its relatively low fusing-point. The finely divided quartz, always present, effects now an increase of fluxing substance, and again an increase in refractoriness, according to the presence or absence of feldspar.

With the plastic less refractory clays (especially the lignite clays) the internal infusibility between clay substance and mineral fragments is much less than in the same components of the kaolins. In respect to the refractory quotient the clay substance of the kaolins ranges from 36.29 to 10.29, as against 8.70 and 3.29 in the plastic clays. That of feldspar may be taken as 1.16. For this reason the influence of feldspar will be less apparent here than in the kaolins; the clay substance, because of its earlier softening, will take a more active part in the vitrification than it does in the kaolins. The quartz, on the other hand, will here act less as a flux than in the kaolins, because the clay will have softened and lost its shape before reaching the degree of heat necessary to induce a chemical action of the feldspar on quartz. Hence, quartz will raise the fire-resisting qualities of a clay relatively more, the lower the clay, as a whole, stands in the refractory scale.

Passing down to the most fusible clays, the brick clays, we find that the clay substance hardly differs in fusibility from that of the feldspathic portion; instances might no doubt be found where the former serves as flux and the contents in feldspar in conjunction with the quartz constitute the rigid frame. Here, at all events, quartz plays the leading part in preserving the shape.

This fact becomes very plain in studying the fusion tests represented in the second table.

Let us institute comparisons between the four similar clays from Greppin, Liegnitz, Kottiken, and Ledetz, all low-grade fire-clays for stoneware, on the one hand, and between the four highly fusible ferruginous brick clays from Rathenow, Bockhorn, Schwarzhütte, and Christiania, which to some extent are manufactured into excellent pavers, on the other.

Tabulating the stoneware clays, as was done with the kaolins, according to their degree of softening in the highest heat employed, the Kottiken clay stands first, and that from Ledetz, the most fusible, last. Let us compare the results with the refractory quotients.

	R. Q. (S.) of clay substance	R. Q. (B.) of whole	Clay substance	Feldspar	Quartz
Kottiken clay	8.70	3.72	2.03	72.21	23.06
Greppin clay	4.63	1.86	1.30	79.42	14.30
Liegnitz clay	3.31	1.07	0.40	46.52	47.48
Ledetz clay	3.29	1.91	0.59	62.03	35.08

From the above it appears that Bischof's method of calculating the refractory quotient, whether applied to the clay as a whole or to the clay substance, does not give a value consistent with experimental results, but that mine fairly shows the relative position of the clays. The necessity of applying the calculation to the separate components is much greater here than with the kaolins. According to Bischof's scale, the clay of Ledetz would rank third, while in fact it occupies fourth place. The test shows what I have formerly emphasized,—that the refractory quality of the major constituent, the clay substance, is the main factor in determining complete softening in heat, and that the mass will soften and slag less in proportion as the quartz increases, because of its thickening and stiffening effect. This is well brought out in the clays of Liegnitz and Ledetz, for the clay substances of each are of nearly the same fusibility, but the first of these contains a much larger portion of quartz.

If we next note the first indications of vitrification, we see that feldspar gives rise to no differences. The amount present does not vary much in these cases; and the question, what would be the result if the amounts varied more, is an open one. Here again it is the clay substance which, by its greater or less fusibility, produces the signs of vitrification.

Tabulating the clays according to ease of softening, and beginning with the one that first shows distinct signs of vitrification, the order is:

	R. Q. (S.) of clay substance	Amount of quartz
Ledetz clay - - -	3.29	35.08
Greppin clay - - -	4.63	14.30
Kottiken clay - - -	8.70	23.03
Liegnitz clay - - -	3.31	47.48

It will be seen that incipient vitrification and the fusibility of the clay substance correspond in the first three clays; and that only the Liegnitz clay forms an exception. This is easily explained by its large amount of quartz, which, by hindering the compacting of grain, acts in a contrary direction to clay substance and feldspar.

Let us in conclusion turn to the brick clays and compare the refractory quotients of their clay substance with the fusibility of the clays as shown by the fusion tests. We begin with the most refractory.

	R. Q. (S.) of clay substance	Quartz Per cent
Brick clay from Schwarzehütte	0.69	50.64
Brick clay from Bockhorn	1.44	44.06
Brick clay from Rathenow	1.21	27.17
Brick clay from Christiania	0.96	18.33

The position of these clays in the scale can no longer be determined by calculating the refractory quotients of the respective clay substance. The manner of obtaining the values is at

fault. It will be remembered that some factors had to be neglected because their value has not been established. These are the comparative fluxing values of alumina and silica, and the number of fluxes, and in what proportionate amounts they are present.

In the case of the refractory clays these factors were justifiably neglected: there the proportion of alumina to silica in the clay substance varies only within narrow limits, and the fluxes are of a very subordinate quantity. The clay substances of the clays of easy fusibility, however, contain amounts of alumina and silica, which vary widely in ratio, and the fluxes, while varying greatly in nature, constitute a large share of the whole. Furthermore, some of the latter, as for instance the iron, may be present in the form of a natural admixture and not in chemical combination.

Here the calculated values will have to be considered more as mere approximations than was done before, and values differing but little can not be looked upon as reliable guides to fusibility. The figures might tell us approximately that the clay substance of the four brick clays is about as fusible as the feldspathic portion.

With this fact as premise, the clay substance and feldspathic portion in each of the four brick clays, would soften almost simultaneously, and the quartz would furnish the rigid frame. This is clearly expressed in the behavior of the clays. Those of Schwarzhütte and Bockhorn are favorably known as suitable for paving brick that stand up well in the fire; they are highest in free silica (not as sand in the common acceptance of the term, but present in a finely divided state similar to clay substance), and as it is least affected by heat, it enables the mass to retain its shape. In proportion as this quartz grows less, the clays lose the property of vitrifying and preserving the form under heat.

Stated in brief the results of the experiments and the theoretical discussions are as follows:

1. To express refractoriness numerically is permissible only on the supposition that all particles of the clay unite to form a single chemical compound; such a number deduced from the figures of the gross analysis can therefore only tell us how the

clay behaves at the close of complete fusion but not at temperatures of mere vitrification.

2. A numerical expression for refractoriness is still admissible for the separate mineralogical components which are chemically homogeneous, and it enables us to estimate the behavior of clays at those lower temperatures that are of prime importance in the industries where the clays are not expected to fuse.

3. Bischof's method of computing the refractory quotient does not express everything that has been established experimentally as to the mutual influence of the elementary oxides present in clays; the one proposed by me and applied only to the separate mineral constituents harmonizes better with the experimental result as far as deductions from it are at all possible.

4. Bischof's values as well as mine are but approximations, since factors essential in the fusing process have not been definitely found and must be neglected in the calculations.

5. The preservation of the shape of clay wares, is pre-eminently determined by the refractory quality of that one component which constitutes the larger portion of the mass and furnishes the stable frame whose interstices receive the molten particles. This frame as a rule consists of the clay substance in the kaolins and fire-clays.

6. A content of feldspar in clay promotes its vitrification. Quartz assists the fluxing action when feldspar is present and also when the temperature has been exceeded at which the clay substance commences to soften; otherwise it adds to the portion tending to preserve the shape. In the fire-clays of low-grade, therefore, quartz no longer acts as a flux but as an aid to rigidity; in the brick clays, whose content of feldspathic matter and clay substance are of nearly the same fusibility, quartz serves primarily and almost exclusively to preserve the shape.

## The Effect of Titanic Acid on the Fusibility of Fire-Clays

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OTTO HENSEL, TRANSLATOR

Titanic acid is often found in considerable quantities in shales and bauxites, and its influence on their fusibility has not been sufficiently ascertained. In its properties closely akin to silica, it easily escapes determination, if not especially looked for; the greater portion is contained in the silica. The fact that it is usually present in but minute quantities and its direct determination a difficult and intricate operation, are likely the reasons why in most clay analyses it is not mentioned as a separate element, although it is certainly present in very many clays.

When the analysis of a bauxite, conducted in our chemical laboratory for the clay industries, showed 6.34 per cent of titanic acid, it was thought advisable to look into the pyrometric properties of this element. The following experiments have been carried out with the assistance of Mr. Cramer. Nearly pure clay substance (Zettlitz kaolin with 98.5 per cent kaolinite) was mixed on the one hand with 5 and 10 per cent silica, respectively, and on the other with equivalent amounts of titanic acid (6.65 and 13.3 per cent), each mixture well ground in an agate mortar, formed into small cones and all were fired together in the Deville furnace. The temperature exceeded the melting-point of wrought iron but did not reach that of platinum. The results were as follows :

1. The Zettlitz kaolin was white, nearly non-porous, edges translucent, shape fully retained, with sharp edges and dull surface.
2. 100 Zettlitz kaolin + 5 silica, snowy white, somewhat absorbent, edges translucent, fracture like china, shape fully retained, surface dull.
3. 100 Zettlitz kaolin + 10 silica, perfectly white, somewhat more absorbent than the foregoing, with translucent edges, almost as dense as porcelain, surface dull.

4. 100 Zettlitz kaolin + 6.65 titanic acid. Cone has bent over to some extent, vitrified appearance of fracture, dull glazed surface, dark bluish gray color.

5. 100 Zettlitz kaolin + 13.3 titanic acid. Test-piece has fused to a dark, bluish gray drop of enamel.

From this it appears that titanic acid does not rank as high in pyrometric respects as silica. At very high temperatures silica must be considered as a sort of flux, but titanic acid is a decided flux at those temperatures where silica still gives openness of texture to the body.

Applied to practice it means that more attention should be paid to the presence of titanic acid in the analyses of fire-clays than has been customary. Even if present in small amounts, it may be of consequence in conjunction with other fluxes.

Characteristic is the dark bluish gray color shown by those pieces that contained the titanic acid. The blue-gray coloration assumed by some clays under severe firing is recalled: the content of iron perhaps, does not alone produce it, for some clays with more iron burn completely white. Whether this is due to small amounts of titanic acid must be left to further investigations.

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### On the Composition and Fusibility of Several Feldspars

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OTTO HENSEL, TRANSLATOR

In work done in connection with the fusibility of feldspars and highly fusible clays, contradictions were found which, on closer study, were aggravated by direct fusion tests, which gave results almost contrary to the law formulated at another occasion with apparent correctness from a series of feldspars. This occasioned the undertaking of the following work.

Before the author found an opportunity to investigate the fusibility of feldspars, Dr. Bischof had published a series of analyses of such, from which he considered himself justified to

draw the following deductions, repeated here in his own words :

1. "The law according to which a value calculated from the chemical composition furnishes the index to the fusibility of a feldspar, and which has now been verified for seven instances, must more and more be considered of general application.

2. "According to this fusibility quotient, feldspars may be divided into two groups, one more fusible or more acid with a higher value, and the other more difficultly fusible, or less acid, and with a lower value.

3. "Variations, especially small ones, within the separate groups, cannot be indicated by the fusibility quotient with sufficient exactness. This applies particularly to the group more difficultly fusible, while in the case of the more fusible group, on the other hand, the agreement of the pyrometric result with the value leaves nothing to be desired."

Without desiring to question the correctness of the observations made by an investigator as conscientious as Bischof, the deductions derived from the experiment and published as a law of universal application, seemed assailable for two cogent reasons. The fusibility value is obtained from the data of the analysis in the same manner as the quotient applied by Bischof to the highly fusible clays. From the ratio of the silica and alumina to the fluxes and that of the silica to the alumina, Bischof formulates a single expression as follows:

$$a \text{Al}_2\text{O}_3 + b \text{SiO}_2 + \text{RO} = a \left( \text{Al}_2\text{O}_3 + \frac{b}{a} \text{SiO}_2 \right) + \text{RO};$$

$a$ , the ratio of  $\text{Al}_2\text{O}_3$  to RO is multiplied by  $\frac{b}{a}$ , the ratio of silica to alumina. But this fusibility value,  $\frac{a \times b}{a}$ , expresses merely the ratio of silica to the fluxes (this seems to have entirely escaped Bischof so far and was shown by me in a former article), while the ratio of the alumina to the fluxes has been eliminated by an arbitrary multiplication and division, and the amount of alumina does not affect the number at all.

According to that law an increase in Bischof's fusibility quotient means a more fusible feldspar but a less fusible clay

(having reference to those not refractory). To assume that materials of similar properties, and often approaching each other in quantitative composition, would exhibit a behavior diametrically opposite, seems strange and one is inclined to doubt his law for the fusibility of feldspars. Aside from this contradiction, Bischof's law would still create doubt as being contrary to practical experience in respect to the fusibility of glasses, which are distinctly analogous to feldspars. Glasses become less fusible with an increase of silica, other things being equal, and his experiments give no support to the assumption that feldspars become more fusible with an increase of silica; furthermore, clays of easy fusibility behave like glasses, and feldspars occupy a position midway between the two.

Hence one is led to suppose that the factors taken into account by Bischof in computing the fusibility quotients, cannot perhaps have been the only determinative ones, but it seems that other points have been overlooked. It is not at all difficult to find at least one, aside from others of some possible influence, and that is the nature of the fluxes present, a point emphasized in the discussion on the refractory quotients of clays. In finding an approximate numerical expression for the refractoriness of clays, especially for the fire-clays, we may neglect that point, as there the amount of fluxes is relatively small, but it is different in the case of feldspars where the fluxes constitute a large percentage of the total. From the analogy of the glasses, drawn before, it is known that fusibility depends not only on the proportion of fluxes to silica, but also on their nature and relative amounts of the different ones. From the very beginning the same influences must be assumed for feldspars. The differences in the nature and amounts of the fluxes that are present in the feldspars examined by me, happen to be more pronounced than was the case in those examined by Bischof; and that may be the reason why the results of the experiment do not agree with Bischof's law.

The feldspars investigated were as follows:

1. Flesh-tinted feldspar from the granite of Chotoun near Prague;

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- 1a. Grayish white, same locality, grown in with the former;
2. Whitish feldspar from Bischofsteinitz;
3. Whitish feldspar from Bischofsteinitz;
4. Whitish feldspar from Hagendorf near Weiden, Bavaria;
5. Norwegian feldspar from Royal Porcelain Works at Charlottenburg.

The chemical analysis of these gave the following results:

	1	1a	2	3	4	5
Silica	62.79	63.21	65.85	64.67	64.80	64.98
Alumina	20.51	22.93	19.38	20.14	19.83	19.18
Ferric oxide	0.47	0.45	0.33	0.25	0.22	0.33
Barium oxide	2.83	0.00	0.00	0.00	0.00	0.00
Calcium oxide	trace	3.62	0.00	0.00	0.00	trace
Magnesium oxide	trace	trace	trace	trace	trace	0.25
Potassium oxide	9.44	1.25	11.18	11.35	11.63	12.79
Sodium oxide	4.08	8.45	3.74	3.58	3.23	2.32
Loss on ignition	0.21	0.59	0.25	0.36	0.67	0.48
	100.33	100.50	100.23	100.35	100.38	100.33

The peculiarities in these analyses are first the high barium content in the flesh-tinted feldspar of Chotoun, to my knowledge never found to such an extent in any other, although a small amount of barium has been proved by A. Mitscherlich to exist in a great many granites; and second, the great divergence of the white feldspar grown in with the first one. According to the kind of fluxes, feldspar 1 is a potash-soda-barium and 1a a soda-lime feldspar. The others contain principally potash with a considerable amount of soda.

Calculating the ratio of the fluxes (including the iron after reducing it to equivalent ferrous oxide) to alumina and silica, according to Bischof's method, we obtain the following figures:

1. RO + 1.05 Al<sub>2</sub>O<sub>3</sub> + 3.61 SiO<sub>2</sub>.
- 1a. RO + 1.02 Al<sub>2</sub>O<sub>3</sub> + 3.17 SiO<sub>2</sub>.
2. RO + 1.03 Al<sub>2</sub>O<sub>3</sub> + 3.90 SiO<sub>2</sub>.
3. RO + 1.07 Al<sub>2</sub>O<sub>3</sub> + 3.87 SiO<sub>2</sub>.
4. RO + 1.08 Al<sub>2</sub>O<sub>3</sub> + 3.97 SiO<sub>2</sub>.
5. RO + 1.01 Al<sub>2</sub>O<sub>3</sub> + 3.86 SiO<sub>2</sub>.

According to Bischof the relative fusibilities would be expressed by

<sup>1</sup>	<sup>1a</sup>	<sup>2</sup>	<sup>3</sup>	<sup>4</sup>	<sup>5</sup>
3.61	3.17	3.90	3.87	3.97	3.86

By Bischof's law, according to which the larger value indicates the more fusible, and the smaller the less fusible materials, we should expect that 1 and 1a would be the most difficult ones of the lot to fuse ; but the result of the test was quite different.

For the fusion test regular tetrahedrons of 2 cm. at the edge were molded from the powdered spar, first with an addition of 10 per cent of Gruenstadt clay as binding material, next with starch paste. They were molded by hand and rubbed down on a ground-glass plate till perfectly plane surfaces and straight edges were obtained. Six of such pyramids were placed in a circle on a plate of fire-clay, covered with a fire-clay bell, and placed exactly in the center of a thick-walled cylindrical muffle. They were then subjected to beginning white heat with coke and forced draught. After several repetitions of firing undertaken to equalize any possible irregularity in the heating, the soda-lime spar 1a proved to be decidedly the most fusible. The trial pieces of this, both those with dextrine, as well as those with clay, had run to a perfectly spheroidal drop of enamel without any resemblance to the original shape. Next ranged the feldspar containing barium, which was much softened, edges and corners having disappeared, but the form of the drop still suggested the original tetrahedron. The other trials had fully preserved their shape, but the mass appeared dense, like porcelain, strongly translucent, slightly glazed, and with slightly rounded corners and edges. Differences between feldspars 2, 3, 4, 5 could not be recognized definitely, a fact traceable to their almost identical composition.

If the silica content of the feldspars alone determined the fusibility, as Bischof's law actually demands, then this test would prove the opposite of what he deems to have established by a series of experiments ; for in this case it is not the most, but the least, silicious feldspars that show the earliest fusion. As ex-

plained in a former article, this is not the only important factor, but there is another factor of great influence, not embraced in the value, namely, the nature of the fluxes present and their proportionate amounts. Scientific investigation gives us no information on this score; we merely know from the experience of the glass industry that potash and potash-lime glasses are more difficultly fusible than soda, soda-potash, and soda-lime glasses, other things being equal, and that as a rule glasses become more fusible with an increase in the variety of the fluxes introduced. Until these influences have been determined by science and the value of each flux fixed, we must be content with comparison by direct tests for the best information obtainable.

For this reason the quotient given by me as being more correct in indicating the fusibility of clays and similar substances, cannot be used for making comparisons. It represents merely an approximate value, for it neglects the nature of the fluxes. The refractory quotients would be as follows:

1	1a	2	3	4	5
1.36	1.35	1.30	1.37	1.37	1.27

and mean only that the fusing-points of the feldspars lie close together, but do not settle the question as to which is the more and which the less fusible.

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### The Determination of Refractoriness of Clays

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OTTO HENSEL, TRANSLATOR

The pyrometric testing of clays is at present (1888) in a stage of transition. Bischof employs a Deville furnace for the test and subjects the specimens to a heat corresponding to the fusing-point of platinum or even higher. Many others, among them myself, have since adopted this furnace for the tests. Its construction as used by me, agreeing with Bischof's specifications

except in some minor details, is as follows: A thick wrought-iron plate, *B*, supports a hollow fire-clay cylinder, *A* encased in sheet iron. Cylinder *A* has a diameter in the clear of 11 cm. and a height of 20 cm. It is continued above in a fire-clay hood, *C*, also encased in sheet iron. Plate *B* is perforated with three concentric rows of holes, *a*, of 5-6 mm. each; in the center is a larger opening, *b*, 30 mm. in diameter. The sheet-iron casing of the furnace extends about 10 cm. below the perforated plate and is closed at the bottom by an iron plate, *D*, supported on three legs. The joint is luted air-tight with clay.

In the lower portion of the furnace is an opening, *c*, for forcing in air by means of a pair of bellows. The air rises into the combustion chamber above through the small holes *a*. The opening *b* receives the plug-like projection of the crucible support *E* and holds it immovable in the center; when firing is finished, it is convenient for removing the ashes into the space below. A crucible of 40 mm. outside diameter and 45 mm. height, centered on the support by means of a little plug-like projection, receives the specimens to be tested, along with the standard clays for comparison; the samples have been molded into small tetrahedrons or prisms (the latter being used by Bischof), and stuck on a small fire-clay disk. Crucible, support, and clay lining must consist of the best refractory material: I employ a mixture of equal parts of Zettlitz kaolin and Neurode shale, previously burned in a porcelain fire and picked over. A piece of platinum always accompanies the specimens in the crucible. Fire is started in the furnace with some glowing charcoal and then the

fuel proper is added. Formerly I followed Bischof in employing crushed coke for that purpose, but for a long time I have been using retort graphite from gas works. I recommend the latter, for it has an advantage in that it leaves less than 0.1 per cent of ash, while coke often leaves more than 10 per cent. The holes of the plate are therefore not so liable to become clogged with cinders, and the crucible is scarcely attacked by them. The latter feature may become extremely disagreeable, especially when very high temperatures are attempted.

The clays to be tested along with the standard clays and a piece of platinum are thus placed in the crucible, and by means of forced draft, a heat reaching the melting-point of platinum is produced. The appearance which the wholly or partly fused specimens present, when compared with the standard clays, enables us to assign them their places on the scale of fusibility. To arrive at definite results, especially to find what standard clays come nearest to those in question, and what temperature is the right one for bringing them to the same stage of fusion, several firings are required; three or four are sufficient, as a rule.

For a scale of fusibility a series of naturally occurring clays were employed by Bischof. They are extensively known from his work, "Die feuerfesten Thone," the shale of Saarau, the Zettlitz kaolin, the clays of Stroud Maiseroul, Mülheim, Grünstadt, Oberkaufungen, and Niederpleis. I also employed these clays obtained from Dr. Bischof, in my tests.

Bischof always utilizes the melting of a bit of platinum wire to a ball as a second indicator of a definite temperature obtained, and he seems to consider this the more reliable of the two. I am inclined to regard this as a sign of uncertain value, and hold that the main device for grading specimens in the scale of fusibility is furnished by the standard clays always placed with the former into the crucible, for platinum, like iron, has the property at a high temperature of absorbing carbon from the fire-gases and thereby fusing at lower temperatures. The difference in the melting-point of iron with a varying percentage of carbon, as wrought iron, steel, and cast iron, is well known, and platinum acts

similarly, depending on the amount of carbon absorbed. I, too, always place a bit of platinum in the crucible, but have observed that at one time the specimens and standard clays showed a more advanced state of fusion while the platinum had not run to a globule and again the clays were evidently less fused, but the platinum had melted completely. The same thing would happen even if I placed it in tiny crucibles lined with pure alumina, as was formerly my practice, so that contact with clay and absorption of silica, which acts like carbon, cannot be the cause of this irregularity.

This may be illustrated by some examples. A brick of the best refractory material is subjected to the highest heat obtainable in a flame of water-gas in the water-gas works of Mr. Blass at Essen, and is found to be much softened. The cone here marked No. 1, identical in composition with cone No. 33 of the table given later on, and corresponding to about clay III of Bischof's standard clays, is fused to a round drop of enamel, but the platinum is not fused. In these crucible tests in one case No. 32 appears fully melted, No. 33 glazed and somewhat bloated with edges still quite distinct, Nos. 34 and 35 have preserved the earthy appearance, and the platinum is not fused. In a second instance Nos. 29, 30, and 31 have fully gone down, No. 32 is glazed and somewhat bloated, the edges begin to become round, No. 33 has sharp edges with surface just glazing, Nos. 34 and 35 are dull, and the platinum is not fused. Finally in a third test, cone No. 30 has fully retained its shape, edges not rounded, barely glazed, Nos. 31, 32, 35, and Bischof's standard clay II, still appear earthy, but the platinum has contracted to a globule. In one case the platinum was not fused while cone No. 33 had fully gone down, in the other the platinum was fused while cone No. 30, much more fusible from its higher percentage of silica, just began to show incipient fusion.

These results are quoted to show the real value of tests for refractoriness at the "controlling melting-point of platinum," and it remains to discuss the second means of determining the place of clayey materials in the scale of refractoriness—the standard clays.

Some time ago when my supply of certain numbers of Bischof's standard clays ran low, I thought of replenishing it, and so applied to him. Unfortunately I could receive nothing from Dr. Bischof. He advised me that he had to be chary of his stock and that he had already been obliged to replace some numbers by other clays of similar composition. I therefore induced Mr. Cramer to work on a new scale for the pyrometric tests. The result of his labors is a proposition<sup>1</sup> to mix a highly refractory clay, in this case Zettlitz kaolin, with varying amounts of powdered marble, and thus obtain bodies of different melting-points. However admirable a series of mixtures differing in melting-point will result, I do not now recommend this method, although it originated with my cooperation. The mixtures contain an element, the calcium carbonate, that differs in fusion from fire-clays, which are naturally free from lime. Such test-pieces fuse very suddenly to a thin liquid condition, while fire-clays fuse much more gradually; therefore the kaolin-lime mixtures are not so well adapted to the tests as the standard clays.

In a recent publication, Bischof has called attention to this valid objection to a mixture of clay and lime, and at the same time has given us a new scale<sup>2</sup> based on mixtures of his most refractory clay of the old scale, Saarau shale, and the least refractory, the clay of Niederpleis. This is a step in advance, for two clays of a definite composition can always be obtained more easily than seven.

But this proposition is not an ideal solution of the problem and as the producers of fire-clay wares and the industries using such have not yet become familiar with it, I must decline to employ and introduce this scale. I am of the opinion that a scale of refractoriness for the testing of fire-clays alone is not good in principle, but that one scale should be made applicable to all in-

<sup>1</sup> See Cramer: "Eine neue Feuerfestigkeits-skala" and "Zur Feuerfestigkeits-bestimmung der Thone." *Thonindustrie Zeitung*, 1887, No. 11, and 1888, No. 12.

<sup>2</sup> See Bischof: "Empirische Berechnungs-skala für die Feuerfestigkeit der Thone." *Thonindustrie Zeitung*, 1880, No. 12.

dustries ; for if every industry will adopt its own scale for the measurement of temperatures, others will naturally be led to measure fire-clays with their standards, and great confusion and errors would be the result. Furthermore the clays proposed by Bischof are not available to many, myself included. Bischof considers it a valuable feature that the percentages of refractoriness be maintained, and in the article has given the proportion of each clay necessary to produce a given value. Aside from the fact that he has not proved by experiment the agreement of the calculated percentages with the old numbers obtained by trial, the nomenclature is vague and for that reason not to be recommended. I therefore attach no value to it. All it teaches is that higher numbers correspond to greater refractoriness, while but few know the full meaning of the values.

Several years ago I originated a scale for the measurement of temperatures by mixing definite amounts of nearly pure clay substance (Zettlitz kaolin), quartz, feldspar, and marble. This was intended to be used in the kilns of the clay-working industries and for much lower temperatures than are required for the present purpose. That they gave no indications at the "controlling melting-point of platinum" but fused much sooner, has subjected me to attacks by Bischof. In the latest one Bischof shows that it is possible for higher numbers to melt first, if by chance they have received higher degrees of heat.

These sallies of theoretical objections to their use, not proved directly, do not exclude the fact that with an increase of temperature they go into fusion in regular sequence, provided care has been taken to place them so that the heat acts upon them in the same manner. Their composition is such that the amount of fluxes decreases progressively, while the ratio of alumina to silica, expressed in chemical equivalents, remains the same throughout. In the lower, most fusible numbers only is the more fusible iron oxide substituted for alumina. The composition of the last ten numbers is as follows :

No. 11.	0.3 K <sub>2</sub> O, 0.7 CaO, 1.2 Al <sub>2</sub> O <sub>3</sub> , 12 SiO <sub>2</sub>	Difference:
No. 12.	0.3 K <sub>2</sub> O, 0.7 CaO, 1.4 Al <sub>2</sub> O <sub>3</sub> , 14 SiO <sub>2</sub>	
No. 13.	0.3 K <sub>2</sub> O, 0.7 CaO, 1.6 Al <sub>2</sub> O <sub>3</sub> , 16 SiO <sub>2</sub>	0.2 Al <sub>2</sub> O <sub>3</sub> , 2 SiO <sub>2</sub> .
No. 14.	0.3 K <sub>2</sub> O, 0.7 CaO, 1.8 Al <sub>2</sub> O <sub>3</sub> , 18 SiO <sub>2</sub>	
No. 15.	0.3 K <sub>2</sub> O, 0.7 CaO, 2.1 Al <sub>2</sub> O <sub>3</sub> , 21 SiO <sub>2</sub>	Difference:
No. 16.	0.3 K <sub>2</sub> O, 0.7 CaO, 2.4 Al <sub>2</sub> O <sub>3</sub> , 24 SiO <sub>2</sub>	
No. 17.	0.3 K <sub>2</sub> O, 0.7 CaO, 2.7 Al <sub>2</sub> O <sub>3</sub> , 27 SiO <sub>2</sub>	0.3 Al <sub>2</sub> O <sub>3</sub> , 3 SiO <sub>2</sub> .
No. 18.	0.3 K <sub>2</sub> O, 0.7 CaO, 3.1 Al <sub>2</sub> O <sub>3</sub> , 31 SiO <sub>2</sub>	
No. 19.	0.3 K <sub>2</sub> O, 0.7 CaO, 3.5 Al <sub>2</sub> O <sub>3</sub> , 35 SiO <sub>2</sub>	Difference:
No. 20.	0.3 K <sub>2</sub> O, 0.7 CaO, 3.9 Al <sub>2</sub> O <sub>3</sub> , 39 SiO <sub>2</sub>	

The melting-point of cone No. 20 corresponds to the highest temperatures required in firing hard porcelain.

If the needs of the clay industries are thus filled, not as regards the testing of clays, but as regards the measurement of temperatures in the larger kiln spaces, it nevertheless soon appeared that other industries employing a much higher heat wished to employ such cones. These industries were the iron and in connection with it the water-gas industries that approached me to assist them in measuring much higher temperatures. I then made additional cones in which I retained the same principles of composition as in the former.

No. 21.	0.3 K <sub>2</sub> O, 0.7 CaO, 4.4 Al <sub>2</sub> O <sub>3</sub> , 44 SiO <sub>2</sub>	Difference:
No. 22.	0.3 K <sub>2</sub> O, 0.7 CaO, 4.9 Al <sub>2</sub> O <sub>3</sub> , 49 SiO <sub>2</sub>	
No. 23.	0.3 K <sub>2</sub> O, 0.7 CaO, 5.4 Al <sub>2</sub> O <sub>3</sub> , 54 SiO <sub>2</sub>	0.5 Al <sub>2</sub> O <sub>3</sub> , 5 SiO <sub>2</sub> .
No. 24.	0.3 K <sub>2</sub> O, 0.7 CaO, 6.0 Al <sub>2</sub> O <sub>3</sub> , 60 SiO <sub>2</sub>	
No. 25.	0.3 K <sub>2</sub> O, 0.7 CaO, 6.6 Al <sub>2</sub> O <sub>3</sub> , 66 SiO <sub>2</sub>	0.6 Al <sub>2</sub> O <sub>3</sub> , 6 SiO <sub>2</sub> .
No. 26.	0.3 K <sub>2</sub> O, 0.7 CaO, 7.2 Al <sub>2</sub> O <sub>3</sub> , 72 SiO <sub>2</sub>	.....(VII.)

It soon became apparent that these cones only partially satisfied all needs and that their range of melting-points was so small as to render the noting of differences in consecutive numbers a difficult matter. I therefore reduced the fluxes still farther and finally omitted them. Thus originated two numbers of the composition

- No. 27. 0.3 K<sub>2</sub>O, 0.7 CaO, 20 Al<sub>2</sub>O<sub>3</sub>, 200 SiO<sub>2</sub>, and  
 No. 28. Al<sub>2</sub>O<sub>3</sub>, 10 SiO<sub>2</sub>, .....(VI).

There remained but one way to raise the refractoriness, and that consisted in gradually decreasing the silica. The following compositions resulted :

	$\text{Al}_2\text{O}_3$ , 9 $\text{SiO}_2$ (7).
No. 29.	$\text{Al}_2\text{O}_3$ , 8 $\text{SiO}_2$ (6).
	$\text{Al}_2\text{O}_3$ , 7 $\text{SiO}_2$ (5).
No. 30.	$\text{Al}_2\text{O}_3$ , 6 $\text{SiO}_2$ (4) .....(V).
No. 31.	$\text{Al}_2\text{O}_3$ , 5 $\text{SiO}_2$ (3).
No. 32.	$\text{Al}_2\text{O}_3$ , 4 $\text{SiO}_2$ (2) .....(IV).
No. 33.	$\text{Al}_2\text{O}_3$ , 3 $\text{SiO}_2$ (1) .....(III).
No. 34.	$\text{Al}_2\text{O}_3$ , 2.5 $\text{SiO}_2$ .
No. 35.	$\text{Al}_2\text{O}_3$ , 2 $\text{SiO}_2$ (0) .....(II).
No. 36.	Rakonitz shale .....(I).

The Arabic figures affixed designate those cones that were employed in a test at the water-gas works of engineer Blass of Essen, all of which went down, the lower numbers to enamel-like masses, the higher ones to more or less transparent glasses, while the strip of platinum placed with them remained unfused. The compositions lying between cones Nos. 28 and 29, and between Nos. 29 and 30 were afterward dropped from the series because differences in fusibility between them and adjoining numbers of the cones were hardly noticeable. Between (0) and (1) I have inserted another number with 2.5 silica, since one whole equivalent of silica proved to result in a very large interval. The Rakonitz shale has been appended as No. 36. The Roman figures approximately represent the position of Bischof's standard clays in the scale.

I do not see why this scale, originally devised for other purposes, cannot be employed in testing the refractory quality of clays. That they represent a scale of fusibility varying with regularity according to number has been proved by numerous experiments, where in each case a large number of them were exposed to the fire. In composition they correspond to naturally occurring clays, for like these they are composed of clay substance proper, quartz, and feldspar, and finally small amounts of calcium carbonate. That they can be reproduced at any time by means of a clay commercially obtainable, which is not the case with Bischof's scale, is to my mind the greatest point in their favor.

I may add that of late I have dispensed with Zettlitz kaolin,

a Bohemian product, and utilized instead a native one of the same composition and refractoriness, likewise consisting of nearly pure kaolinite (1 per cent quartz), and obtained from Grünstadt in the Palatinate, through the kindness of Messrs. Schiffer and Kircher. That the scale is accessible to any one and that every manufacturer is thus enabled to conduct his pyrometric tests for himself, is another advantage over Bischof's series.

The melting-points of the lower numbers of the series have been expressed in degrees of the thermometric scale, but I have been obliged to make many hypothetical assumptions. I have assumed that the series with cone No. 1 begins at 1150°, and reaches the highest temperature obtainable in the porcelain kiln with cone No. 20, a temperature assumed at 1700°; and that furthermore all cones represent equal intervals of fusibility. Thus I have interpolated the degrees. I must say that I have reluctantly done so, in obedience to pressure from manufacturers and that I must always make reservations in regard to these thermometric degrees. But for the highest numbers I do not venture to follow the same plan, for lack of tangible data. Once accustomed to designate temperatures by cone numbers, one will find them adequate even if they represent an expression differing from the customary notation. For instance let it be stated that a clay comes up to cone No. —, and a definite fusibility is thus expressed and the same point can always be found in the future. It will be unnecessary to add degrees impracticable to verify by direct tests.

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### Relations between Plasticity and Refractoriness of Clays

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OTTO HENSEL, TRANSLATOR

Plasticity is a very important property of the materials with which we work. It is the specific property enabling us to work clays in the customary manner. Plasticity enables solids to receive a liquid into their pores, to retain the latter completely,

thus enabling the mass, by pressure and kneading, to take any desired shape, to retain the shape unchanged on the removal of pressure and extraction of the liquid and the consequent change to the solid state. It is not found in all friable solids; many cannot be molded when mixed with a liquid, or on its removal will not possess sufficient cohesion of the particles to result in a strong body.

The degree of plasticity of clayey masses, always representing mixtures of granular non-plastic portions and the really plastic element, clay substance, or kaolinite, depends on the relative amount of these components. Still we know that clay substance proper exhibits marked variations of plasticity even with identical chemical composition. One clay substance is short, may be mixed with but small additions of non-plastic material if plasticity is to be retained, and dries to a loosely cohering body; the other is very fat and may be diluted with a large amount of non-plastic portions without loss of its capacity to take shape by molding, and to dry to a hard, very tough mass. The former variety is mostly identified with those materials found on the primary site and having their origin in the weathering of feldspar (namely, the kaolins) while those clays that have passed through a natural washing process, commonly known as plastic clays, develop plasticity to a much greater extent. What the cause of this difference is, whether due to much finer subdivision in the washing process, or whether the second variety is derived from rocks other than feldspar, is an open question; we have still to take into account that materials differ in their degree of plasticity. With these differences of plasticity we deal in the composition of bodies and in their molding, but they are also of importance at the next stage (the burning of the ware), because here diversities spring up that are directly due to variations in plasticity. To these diversities originating in the burning, which up to the present have been somewhat slighted, I wish to call particular attention.

There is a connection between plasticity and the hardness that clays acquire on drying. On examining bodies made up

in exactly the same proportion of constituents, now with a plastic clay, and again with one of low plasticity (a kaolin), we note that the particles in the more fragile composition are arranged more loosely while the harder body obtained with the plastic clay is denser. This becomes plain when two clays of almost identical chemical composition, but of different degrees of plasticity, are compared. Let us take Zettlitz kaolin and the clay of Mülheim near Koblenz. Providing the former is washed, both contain but a small amount of quartz fragments, only about  $1\frac{1}{2}$  per cent in either; the remainder in each is nearly pure clay substance ( $\text{Al}_2\text{O}_3$ ,  $2\text{SiO}_2$ , +  $2\text{H}_2\text{O}$ ) and shows only a small difference in iron oxide of about 1 per cent. Bodies obtained from these by the ordinary process of soaking, molding, and drying, will differ greatly in porosity and hardness.

Clays of Zettlitz kaolin are friable and have a porosity of 42 per cent, while those of Mülheim clay are very hard and have a porosity of only 28 per cent; therefore they are denser. Both subjected to heat, the Mülheim clay will have acquired a dense, non-porous structure relatively early, far below its fusing-point and a little above that of gold, somewhere at  $1100^\circ$  to  $1150^\circ$ , while the kaolin remains porous up to a high heat. This density of structure in the plastic clay can not at all be considered as incipient vitrification; the clay remains in this state up to a very high temperature, and may be classed as a very good refractory material. This change to a denser structure must rather be conceived as a closer arrangement of the molecules of the substance, and is probably connected with the closer molecular arrangement of the smallest particles in the drying stage. Those clays that are plastic, and dry to a hard, tough mass, behave like the Mülheim clay in exhibiting a much earlier vitrification to dense impervious bodies; this becomes especially striking when they are fired with kaolins that become dense much later, even when less refractory than the plastic clays. This peculiarity is realized where it is desired to produce dense, non-absorbent bodies from fire-clays, as for instance in the manufacture of floor tiles and where it is necessary to produce refractory articles that shall resist the action of liquids at very high

temperatures, a problem met with in the production of glass pots and the like. Looking over the line of clays employed in those specialties, we find that medium grade fire-clays of high plasticity preponderate over those of highest refractoriness. Those used specially for glass pots (the Belgian of Straud Maiseroul, that of Hettenleidelheim, of Klingenberg, of Grossalmerode, and others) are such which early acquire great density because of their high plasticity, and are therefore less attacked by the glass than if the pots were made of a kaolin more refractory, but retaining an open structure. Because of their early density, the former resist the effect of fluxes for a much longer time than those which remain porous at high temperatures and permit fused substances to penetrate into the interior of the mass. We are thus able to offer greater resistance to specific influences of the kiln contents with less refractory clays if they become dense relatively early. Frequently, the refractory materials withstand the action of heat alone very well, if the gases are unaccompanied by the alkalies of the ashes (vapors of common salt in short); because of small amounts, these various influences do not attract notice in analyses, but show their presence by their action on the lining material. Years ago a gentleman asked me for advice in reference to material for crucibles employed in the manufacture of glass ware. Although he was sure of having selected material of the highest refractory value, it soon showed indications of a short life. At that time I did not attach much weight to the rate at which fire-clays acquire a dense structure, but now I am convinced that the trouble must be explained in that way. Something similar will take place in the coke ovens, for instance, which on account of the temperature employed do not require material of highest refractoriness. Several years ago Dr. Otto showed that in this industry the vapors of common salt arising from the coal have a large share in the destruction of the refractory material. Here, as in many other industries, it will be necessary to make use of a grog which is very hard and dense. Such grog can always be obtained more easily if burned from very plastic clays instead of

kaolins, loose-grained though frequently more refractory. It will thus be easier to obtain bodies very dense, and therefore of longer resistance.

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### The Chemical and Mechanical Analysis of Clays and the Interpretation of the Results Obtained

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OTTO HENSEL, TRANSLATOR

In the chemical examination of clays it will always be necessary, if great errors are to be avoided, to adopt a method that will with certainty lead to the desired end. Such an analysis has for its object the determination of a number of substances characterized by sharp and reliable reactions. Exact results are only possible if one is guided strictly by these reactions. The chemical analysis of fire-clays requires a determination of the following substances: Silica (including titanic acid), alumina, ferric oxide, lime, magnesia, potash, soda, and loss by ignition.

Other substances present either rarely or in minute quantities generally need not be determined, and therefore, I omit them. These are: manganic oxide, vanadic acid, lead oxide, cobalt oxide, etc. I will say that, wherever possible, it is always best in analyzing clays to use platinum vessels, as the ordinary glass vessels introduce grave errors in the results. Some of the glass is always dissolved in boiling and decomposed by the boiling water and its elements being precipitated along with those of the clay commonly give too high results in silica, lime, and the alkalies. Although measuring flasks cannot be dispensed with, the boiling and especially evaporation of liquids in glass vessels is to be avoided. To determine the loss by ignition, 1 to 2 grams of the material are weighed in a platinum crucible and heated to redness. The operation must be finished over the blast-lamp at very high heat to make sure of driving off all of the water, and should be repeated to constant weight, as the

expulsion of the last traces of water in fire-clays, especially, is not always an easy matter.

For the determination of the silica and titanic acid the substances must first be brought into a form to dissolve completely in dilute hydrochloric acid. From 1 to 2 grams of the material is weighed out in a platinum crucible and covered with four to five times its weight of a mixture of potassium and sodium carbonates; when it is very aluminous it is well to take eight times its weight as otherwise the fused mass becomes too viscous. The mixture is subjected to a high temperature, say the melting-point of silver; the alkali carbonates fuse and with the clay form compounds easily soluble in acids. The fusion must be continued only till the mass is perfectly liquid and the evolution of gas has ceased; a further heating is to be avoided as otherwise double silicates will segregate, and these are decomposed and dissolved with difficulty. The fused mass, having been softened with water to a voluminous mass of alkali aluminates and silicates, is dissolved in hydrochloric acid. If the clay has been properly unlocked by the alkali carbonates, a perfectly clear solution will result; this must at all events be obtained if correct results in silica and titanic acid are desired.

To obtain the silica and titanic acid in the solution, this must be completely evaporated to dryness, whereby they change to an insoluble hydrated form. This is accomplished on the water-bath, lastly in the air-bath at  $120^{\circ}$  till no hydrochloric acid is perceptible to the smell and a perfectly dry mass of salts is left, which contains the silica and titanic acid in an insoluble form. The mass is next moistened with concentrated hydrochloric acid, allowed to stand about fifteen minutes, then diluted with some water, heated on the water-bath for a while, then rinsed on to a filter and washed with hot water till the last washings tested with silver nitrate no longer react for chlorine. The residue of silica is placed, while moist, into a platinum crucible, heated cautiously till the filter is well charred, then strongly till the same has become white, and finally over the blast-lamp. The ignition over the blast-lamp must be repeated several times till

the weight is constant. Attention to this is necessary if reliable results are desired, for the last traces of water are removed with difficulty.

If any titanic acid was present, it has been weighed with the silica; to determine the amount, the residue must be moistened in the platinum crucible with a few drops of sulphuric acid and then pure hydrofluoric acid solution poured over it. The silica will evaporate as silicon fluoride; the titanic acid will remain as a small residue to be weighed after ignition. However, the result can only be depended on if the unlocking of the clay was complete and was completely dissolved in the acidified solution; otherwise if ever so small a residue is detected, there remains the danger that a small portion of alumina is included, which would also appear here, as it will not volatilize with hydrofluoric acid. The residue must, therefore, be tested before the blow-pipe for titanic acid. In the reducing flame titanic acid gives a violet color with microcosmic salt.

The filtrate from the silica contains the total alumina. As a rule this is too large in amount for determination, since the washing of a large bulk of alumina is very difficult because of its gelatinous nature. Therefore only a portion of the liquid is employed. If the filtrate was collected in a half-liter flask, filled to the mark with distilled water, the whole well shaken and 200 cc. taken for the determination, then 0.4 of the weighed substance is being analyzed. The 200 cc. taken are heated to boiling, preferably in a platinum dish, ammonia is added in small excess, and the ammonia expelled on the water-bath. The alumina and ferric oxide fall down completely. They are filtered off, dissolved in hydrochloric acid, and again precipitated as before. The repetition is necessary because the first precipitate has entrapped some of the alkaline salts that abound in the solution. The precipitate is well washed with hot water on a filter and ignited to constant weight. To find the quantity of iron present, a second 0.4 of the original filtrate is taken, concentrated sulphuric acid added, and heated on a water-bath till the smell of hydrochloric acid has entirely disappeared. The

liquid is then poured into an Erlenmeyer flask ; a piece of pure zinc and a bit of platinum are added, whereby the iron is reduced to ferrous oxide. This is then titrated with potassium permanganate whose titer may indicate about 1 mg. ferric oxide to 1 cc. of the reagent. The quantity of ferric oxide thus found is subtracted from the combined weight of alumina and iron to find the alumina present.

The alkaline filtrate from the determination of the alumina and iron oxide is treated with ammonium oxalate and allowed to stand for some time in a warm place ; the precipitated calcium oxalate is then filtered off, and after severe ignition weighed as calcium oxide. If the quantity is large the ignition must be repeated to constant weight.

The magnesia may properly be determined in the filtrate from the calcium oxalate by adding a large portion of ammonia, equal to about one-quarter of the volume of the solution, and precipitating it as ammonium magnesium phosphate by sodium biphosphate. After standing for forty-eight hours the precipitate is filtered and washed with dilute ammonia, ignited in a porcelain crucible, and weighed as magnesium pyrophosphate ( $Mg_2P_2O_7$ ).

The alkalies cannot be determined in the substance taken for the silica determination, as that was fused with alkali carbonates. Another quantity of the substance must be employed. This is decomposed with pure hydrofluoric acid after the addition of a small amount of concentrated sulphuric acid. One to two grams of the substance will do.

The clay is first soaked with a little hot water and about 1 cc. concentrated sulphuric acid in a large platinum crucible or small platinum dish, then digested on the water-bath with hydrofluoric acid solution. If not many large quartz grains are present, the decomposition is generally rapid ; clay substance and feldspathic matter especially dissolve readily. Large quartz grains remain undissolved, but that does not affect the result. After the silicic fluoride and hydrofluoric acid have evaporated, the dish is set over the burner till sulphuric acid fumes appear.

The residual salts are then dissolved in water and heated to effect complete solution, then ammonia in excess and a few drops of ammonium oxalate are added in order to precipitate the alumina, ferric oxide, and lime. The cloudy solution is poured into a liter flask having a stop-cock on its side, and is allowed to become clear. Then half a liter of the liquid is drawn off, filtered, and the filtrate evaporated to dryness in a platinum dish. Thus one-half of the total alkalies of the substance taken is determined. It would be tedious to filter and wash the large amount of alumina always obtained here; hence it is always better to avoid it in the above manner.

The solution in the platinum dish must be heated to redness to drive off all of the ammonium salts; this is necessary to separate the magnesia in the next step. The residue is dissolved in the least possible amount of water, treated with Schafgott's solution (ammonium carbonate and ammonia) and allowed to stand for twenty-four hours. The magnesia separates as a crystalline precipitate that must be washed with Schafgott's solution. The filtrate and washings are united and evaporated to dryness in a platinum dish, the residue heated to redness, again dissolved, a few drops of ammonia added, filtered, and the filtrate evaporated to dryness. Thus all the alkalies are obtained as sulphates, which after ignition can be weighed. To find the potassium in the combined alkalies, these are dissolved in dilute hydrochloric acid, and sufficient platinic chloride solution of known strength is added to change all the alkalies present to platinum chlorides. The mixture is then heated in a porcelain dish almost to dryness, effecting a separation of the potassium platinichloride. A mixture of 3 parts absolute alcohol and 1 part ether is poured on the thickened mass; the sodium platinichloride will go into solution, while the potassium salt, remaining undissolved, is caught on a filter, and washed with the ether-alcohol mixture. The filter with the precipitate is placed in a Rose crucible and mildly ignited in a stream of hydrogen, whereby it separates into metallic platinum and potassium chloride. The latter is removed by washing, and the platinum

weighed after ignition. From the amount of platinum obtained, the corresponding quantity of potassium sulphate is calculated and subtracted from the total alkaline sulphates. From these data the potash and soda as oxides can then be calculated.

With the determination of the oxides present in clays the investigation, however, is not complete. Clay is a mechanical mixture of substances, not a chemical combination of them, as is well understood, and the above determinations do not reveal them. Resulting from the weathering of feldspathic rocks, clays, as a rule, still contain feldspathic fragments and quartz in greater or less amount.

There is always present a definite combination of alumina and silica, designated by me as clay substance with the composition of  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ .

Admixed quartz and feldspathic fragments, the latter always rich in fluxes, induce fusion of the clay substance and their presence and quantities must be determined.

The quartz present in clays acts as a flux only if present in a state of subdivision so fine that it cannot be separated by washing and can readily enter into chemical combination with the clay substance in burning. If present in the form of coarse grains, merely a superficial combination with clay substance will ensue, with low fluxing energy, as the interior of the grains is debarred from reacting on the clay. Whether coarse grains are present in clay will always be determined by a washing process. 250 grams of clay are soaked in water for this purpose and passed through a fine wire screen of 5000 meshes to the square centimeter (about 180 meshes to the linear inch); flowing water and brush must aid in getting all of the clay substance through. The residue on the screen is collected in a dish, dried and weighed, and can be further sorted by coarser screens or elutriation. The sand that has gone through the screen may be considered of sufficient fineness to combine chemically with the clay substance. The fine sand mixed with the clay substance is separated from the admixed clay substance, and the amount of feldspathic detritus also ascertained, by boiling the total fine substance with sul-

phuric acid—the rational analysis. By the aid of this process a fair conception of the grouping of the oxides in the clay can be obtained. While the clay substance proper, the binding element of clays, is dissolved by boiling with dilute sulphuric acid, the fragments of orthoclase and quartz are hardly attacked at all.

We proceed by boiling 5 grams of the fine clay, screened as above, with about 100 to 200 cc. of water in a platinum dish till it becomes of a soft slimy consistency, cooling, and adding 50 cc. concentrated sulphuric acid, covering with a watch-glass, and boiling over the open flame till the acid begins to volatilize strongly. The clay substance will have been decomposed into aluminum sulphate and hydrated silicic acid. The aluminum sulphate being soluble in water and easily washed out, it remains to remove the separated silica. For this purpose the larger portion of the sulphates is removed by decantation, and the residue boiled with dilute solution of sodium hydroxide to change the silicic acid to a soluble form. It is then filtered, the residue washed back into the dish and boiled with dilute hydrochloric acid, left to stand till clear, the supernatant liquid decanted, the residue again heated with the solution of sodium hydroxide, filtered, and again digested with hydrochloric acid. The solid particles caught each time on the filter are washed back into the dish. This treatment removes the amorphous and hydrated silicic acid obtained in the decomposition of the clay substance completely, while the admixed quartz and feldspathic detritus remain unaltered. These are caught on a filter, ignited and weighed, then digested with hydrofluoric acid and a few drops of sulphuric acid. All the silica now volatilizes as a fluoride while the alumina of the feldspar remains as a sulphate, determined by means of ammonia, after being dissolved in water. A unit of alumina by weight corresponds to 5.41 units of feldspar (orthoclase); we are thus enabled to calculate the quantities of feldspar and quartz originally present.

The question whether a definite conclusion as to refractoriness can be drawn from the data of the analysis can be affirmed

only with some reservations. Years ago Bischof endeavored to draw such conclusions by establishing his refractory quotient. For this purpose he calculated the equivalent proportion between the fluxes (these being equal to unity), the alumina and the silica, and from this he calculated a value which he called the refractory quotient, calling the ratio of the chemical equivalents between the fluxes and alumina  $a$ , the ratio between the alumina and silica  $b$ , then the refractory quotient (R. Q.) is expressed by

$$\text{the formula } \frac{a}{b} = \frac{a^2}{b}.$$

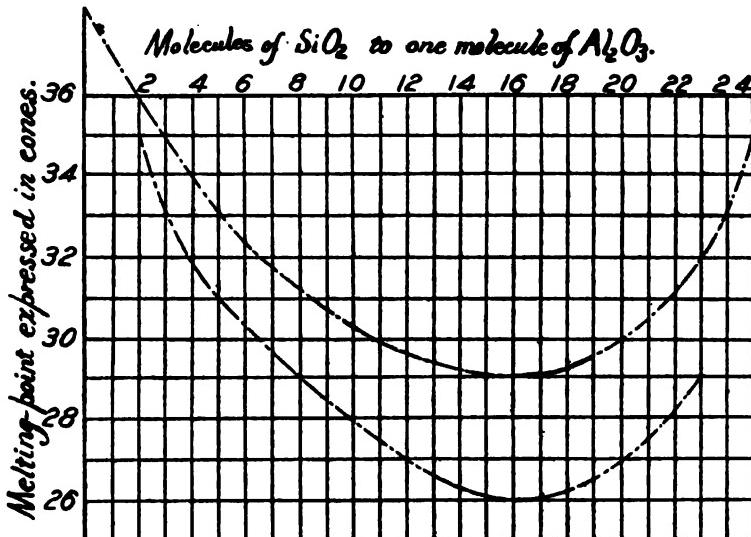
Later I thought best to express the same quotient by the formula,  $(a + b) \frac{a}{b}$ . An expression is thus obtained which is supposed to increase with the rise in refractory power; still I should not attach undue importance to this numerical expression and range clays by it, for one factor has been omitted, namely, the size of the grain of silica—a factor as significant in respect to refractoriness as chemical composition.

It must always be borne in mind that clays are not homogeneous bodies and that the character of the components has a large share in fusion. The refractory quotient can give only an approximate expression to refractoriness. It is best, therefore, to test clays by a direct fusion test in addition to a chemical investigation.

I have of late discarded the fire-clay lining for the Deville furnace, and employ magnesite or chromite instead. Firing is conducted with retort graphite and forced draft. The small crucibles for receiving the specimens can also be made of magnesite or chromite and lined with a layer of finely ground sintered alumina in order to avoid reaction of the basic materials on specimens of silicious clays. In conducting tests at very high temperatures, up to cones 35 and 36, crucibles made of these basic materials are preferable as they will not fuse, unlike the fire-clay formerly in use.

It remains to determine how the chemical constituents affect the refractoriness of clays. First I wish to revert to an

older investigation by Bischof, where he endeavors to ascertain which of the constituents of clay is the most refractory. He tested both alumina and silica and found that the former is the most refractory, and silica but little less so. Mixing silica and alumina in various proportions he found that the composition  $\text{Al}_2\text{O}_3 : 2 \text{SiO}_2$  was the most infusible. This ratio is found approximately in Rakonitz shale and in Bischof's standard clay I. With further additions of silica the fusibility increases and passes beyond that of pure silica. I have represented the facts graphi-



cally where the horizontal coordinates represent degrees of temperature as estimated by my pyrometric cones and the vertical abscissas the ratios of alumina and the admixed alkalies, to the silica expressed in chemical equivalents. The upper dotted curve represents the fusibility of mixtures of pure alumina and silica. It shows that increased silica brings on greater fusibility until the composition  $1 \text{Al}_2\text{O}_3 : 17 \text{SiO}_2$ , in chemical equivalents, is reached and that with further increase of silica the refractoriness rises. The lower curve shows the refractoriness of mixtures obtained by adding sand to Zettlitz kaolin to which a small amount of

feldspar has always been added in order to maintain the proportion of alkalies in the same amount.

The curves show that in clays the composition  $1\text{Al}_2\text{O}_3, 2\text{SiO}_2$  is the most refractory and reaches cone No. 36, or when accompanied by a small amount of alkalies, cone No. 35; and that the fusing-points fall until the composition  $1\text{Al}_2\text{O}_3, 17\text{SiO}_2$  is reached. When the content of alumina has become 0, the refractoriness rises to cone No. 35, the melting-point of pure silica, or crystallized quartz. Compositions containing fluxes, like the Zettlitz kaolin, stand somewhat lower in the scale.

Further experiments have demonstrated that we are able to fuse even the most refractory clays and pure quartz in the Deville furnace; magnesite and chromite could not be fused in it.

The position of a clay in the refractory scale depends not merely on the ratio of alumina to silica, but mainly on the amount of accompanying fluxes, iron oxide, lime, magnesia, potash, and soda. Richters' experiments in this line are not altogether conclusive. He states that they exert the same fluxing value, molecule for molecule, and that therefore, 40 pounds of magnesia, combining weight 40, are equal in fluxing value to 160 pounds of ferric oxide, combining weight 160. My experience seems to show that the iron is rather the strongest flux found in clays. As has already been stated, the silica must be present in a state of great fineness in order to enter into combination. If present as coarse particles, it decidedly tends to raise the refractory value of clays.

Not merely is its resistance to high temperatures of importance in the application of a clay in the industries, but in most cases also its resistance to chemical influences. It does not follow that both properties go hand in hand, and it is frequently seen that a higher grade of fire-brick has a shorter life than a much lower grade. What material is best in each case must commonly be left for practical experience to determine, for science often fails to ascertain the influence of substances acting on it. A case in point is the action of slags and cinders on the

brick-lining of furnaces. It may be stated in a general way that basic slags require basic brick to prevent rapid destruction of the lining, and conversely silicious slags such that are high in silica. Different materials will frequently be required for the various portions of a structure. If for instance the material to be fired is basic, a basic bed must be chosen, while the crown had best be of a silicious material to withstand the action of the flying dust, according to the nature of the latter.

Not only the nature of the substances coming in contact with and reacting on the masonry, but also the physical condition of the latter, bears strongly on its durability. Especially of importance are the hardness to which the material has been burned and the density it has thus acquired. In a general way it may be stated that greater hardness of burning before use, insures better resistance to the chemical influences of the contents or charge. An instance is furnished by the glass industry where clays lower in the scale but burning readily to a dense body resist the action of the charge much longer than highly refractory kaolins that remain porous up to very high temperatures, allow molten glass to penetrate the body, and are rapidly destroyed in consequence.



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